RESPONSE TO THE EDITOR

We would like to thank the editor for the comment regarding Figure 3.

We changed the three panels of Figure 3 to a single panel containing all 3 trajectories. We changed the duration from 96 to 72 hours, since HYSPLIT model graphic design supports maximum 72 hrs run for multiple trajectories in the same figure. However, there is no change in the observations we describe. Accordingly, the caption of Figure 3 was changed to:

"Three-day back trajectories for air masses arriving at Finokalia on 29, 30 and 31 August, 2012."

RESPONSE TO THE REVIEWERS

We would like to thank the reviewer for his/her positive and useful comments. Our answers and actions to the comments are given in italics after each comment.

Anonymous Referee #1

Received and published: 14 May 2015

The paper by Kalivitis et al. presents CCN measurements as well as aerosol chemical composition data from the Eastern Mediterranean marine boundary layer. It leads to the conclusion that the condensation of gaseous sulfuric acid and organic substances onto newly formed particles induces their growth to particle sizes that are relevant for the activation into cloud droplets.

The information given in this manuscript is relevant for the readers of ACP and of interest for the community in general. However, there are a few issues as detailed below that have to be addressed by the authors before I can recommend the paper for publication in ACP.

I have basically problems with the presentation of results in the figures. The authors draw a lot of conclusions from their measurements but they are not nicely represented in the figures. Improving the figures could make it much easier for the reader to spot the points that are made in the text. At the moment, I am not able to follow every conclusion because the figures not necessarily illustrate them.

Therefore, in the following, I raise several questions and suggest improvements (including technical corrections) for a revised version of the figures:

REF:Fig. 1: unit of the flow rate is “cmˆ3 minˆ-1”

ANS:We apologize for this oversight. Corrected.

REF:Fig. 2: Please indicate in the caption what the arrows in the figure mean.

ANS:We changed arrows into dashed lines and added the following text to the figure caption:

“The dashed vertical lines in the figure indicate the times when newly formed particles started to appear to the measured size spectra during the three NPF events concentrated in our analysis.”

REF:Fig. 4: Here it would be good to make two panels out of it, one showing the data for 25

– 28 August and the other for the period after the NPF event. At the moment no clear distinction between the two data sets is possible. You should show the regression lines for both periods as well as the fit parameters and correlation coefficients. Alternatively, they could also be listed in a table for easy comparison. Btw, the color of the equation for the N130 data set shown in the legend does not match the color of the symbols.

ANS:We split the data into two sub-figures, as the reviewer suggests, and made separate regression lines for these subsets of data. The caption of Figure 4 was modified into the following form:

"Relation between the total number concentration of particles with diameter larger than D, N_D, (D = 90, 100, 110, 120 or 130 nm) and measured CCN number concentration at the supersaturation of 0.2 %. The data are from two periods in 2012: from 25 August at 23:05 to 28 August at 10:45 (panel a) and from 1 September at 23:15 to 2 September at 17:15UTC+2 (panel b)."

The text referring to Figure 4 was modified accordingly.

REF:Fig. 6: Please mention that the mass concentrations in panel a are PM1 masses.

ANS:The caption of Figure 6 was modified into the following form:

Time evolution of the aerosol chemical composition during the period 28 August – 2 September 2012. Left panel: absolute concentrations (µg m^{-3}) in the PM_1 fraction of the measured aerosol, except for EC which was measured in the PM_{10} fraction . Right panel: relative contributions to the non-refractive PM_1 mass

REF:Fig. 7: As in all other time series and diurnal cycle plots the x-axis label is missing. Is it local time? Also in this figure one panel showing the mass fractions rather than concentrations would certainly make sense. I am not sure if Fig. 7a (diurnal cycle as an average over the whole August to September period) is telling you anything if you want to explain the chemical composition during the NPF event and possible implication on cloud droplet activation during NPF events.

ANS:The time in the x axes of Figures 7, 8 and 9 refers to local winter time (UTC + 2 hours). We added the label "Time (UTC + 2)" to x axis of these figures. For the figures representing time series, we added the label "Date".

The purpose of Figure 7a is to support our analysis on how primary and secondary aerosol components behave over a diurnal cycle at this site during this time of the year. Therefore, we feel it is important to keep Figure 7a in the paper. Figure 7b then shows the same aerosol components behaved during the time period of most active NPF.

REF:Fig. 8: In this figure the diurnal cycle of kappa is averaged over a different time period than the chemical composition in Fig. 6. How are you able to find a link between these parameters, if you compare apples and oranges? What do you mean with “normalized into the range [0, 1]”? I do not understand how you get from the values in panel a to b. I would have expected that you divide each data point of the diurnal cycle by the average kappa value measured at this diameter. This at least should give you the relative diurnal variation, but in this case the data points would be also larger than one.

So, I simply do not understand the calculation of kappa(normalized).

ANS:Figure 6, like the figures representing either time series (Figures 2 and 5) or diurnal cycles (Figures 7 and 9) of directly measurable aerosol properties, cover the period from 28 August to 2 September. The size-segregated CCN measurements were not available after 22:55 on 30 August, and for this reason Figures 8, 10 and 11 do not extend to the end of 2 September. There was a typo in the captions of Figures 7, 9 and 11: it should read 28 August not 29 August. These dates were corrected in the figure captions.

We clarified this timing issue by adding the following sentence at the end of section 2.2:

“During the study period concentrated in this paper (28 August to 2 September 2012), size-segregated CCN measurements were not available after 22:55 on 30 August, and the total CCN concentration measurements at the 0.2% supersaturation initiated at 23:15 *on 1 September.”*

Figures 6 and 8 are not directly comparable anyway, as the first one represent time series and the second one diurnal cycles.

The scaling procedure in Figure 8b was revisited; we repeated the scaling once again by forcing the average value of each quantity to be equal to unity. We added the explanation of this procedure to the caption of Figure 8 and in paragraph 3.2

“In Fig.8a the daily variation of the hygroscopicity (κ parameter) of 60−120 nm particles averaged over two full days is presented and in Fig. 8b the corresponding normalized values to the average κ of each diameter”

REF:Fig. 9: What exactly is plotted here? The individual organic components as fractions of the total organic mass? Please clarify in the caption and/or y-axis label.

ANS:Correct, they are the fractions of individual organic components of the total organic mass. We clarified this by modifying the figure caption into the following form:

"Diurnal variability of the three major classes of organic aerosol obtained from the PMF analysis, along with the O/C ratio, during the period 28 August to 2 September. The quantity f(OA) represents the fractions of individual organic compounds of the total organic mass, where OA refers to OOA, OOA-BB or α-pinene SOA."

The scale of the left y-axis in our original figure was also modified to reflect the current dataset.

REF:Fig. 10: Here the legend is missing! Again, the plotted time period is different from the periods shown in the other plots (Figs. 5-9). For better comparison the x-axis range should be extended. I guess it would also make sense to present the diurnal cycle of the maximum activation fraction.

ANS:The diurnal cycle is added as Figure 10b. The legend is now added (Fig. 10a in the revised paper), in addition to a figure displaying the diurnal cycle of the maximum activated fraction (Fig. 10b).

The issue of having different time periods in different figures have been addressed in our response to the referee comment on Figure 8.

REF:Fig. 11: This is just another time period you concentrate on. Why not showing an average over all days?

ANS:The issue of having different time periods in different figures have been addressed in our response to the referee comment on Figure 8.

We would like to thank the reviewer for his/her positive and useful comments. Our answers and actions to the comments are given in italics after each comment.

Anonymous Referee #2

Received and published: 28 April 2015

General comments:

I recommend to publish this paper upon minor revisions.

The paper present very important findings to be able to understand how important new particle formation in marine areas is for CCN concentrations. Only superficial attempts have been made previously to elucidate this matter. English language is very clear.

The abstract is short and to the point. The Introduction clearly presents the problem issue at hand, and clearly formulates what measurements are available the research questions addressed. Short and to the point sufficiently described method section. The result section is also condensed, and only accounts for the most important findings.

One discussion topic is omitted in the conclusions section (see below), but otherwise very useful conclusion for future research in this area, where future needs are clearly described.

REF:Specific comments:

Abstract:

”(0.2–0.4 lower kappa between the 60 and 120nm particles)”. Unclear sentence, please rephrase.

ANS:*We modified this sentence as follows:*

"Sub-100 nm particles were found to be substantially less hygroscopic than larger particles during the period with active NPF and growth (the value of κ was lower by 0.2–0.4 for 60 nm particles compared with 120 nm particles), probably due to enrichment of organic material in the sub-100nm size range."

REF:Introduction:

"The probability by which an aerosol particle acts as a CCN at a given supersaturation depends primarily on its size and secondarily on its chemical composition (Dusek et al.,2006). The aerosol chemical composition may, however, have large impacts on the total CCN number concentration (Karydis et al., 2012; Padró et al., 2012)." Contradictory statement. In the first sentence you say that chemical composition influence CCN, and in the second sentence you write that, chemical composition may HOWEVER have influence on CCN.

ANS:*These are not contradictory statements as the first one refers to a single particle and the second one refers to a particle population. However, in order to avoid confusion, we reworded the second sentence into the following form:*

"In a population of aerosol particles, the total CCN number concentration is affected by the chemical composition and mixing state of these particles."

REF:Chapter 2.2.

Page 1148. How was the BC concentration determined from the absorption coefficients? Please write if you made some kind of own corrections, or used the corrections found in other literature, or if you just used the BC values that the instrument spits out without further correction.

ANS:*The aethalometer data were corrected according to Weingartner et al., 2003. The following sentence was added in paragraph 2.2:*

" Aethalometer data were corrected using the empirical formula given by Weingartner et al. (2003). In this formula (their equation 4), the calibration constant C has been calculated to be 2.48 for the Finokalia station in summer and R(ATN) was taken as 1, the value representative for aged particles at remote locations (Sciare et al., 2008)."

REF:Page 11149, line 2. "this" should be replaced by "which".

ANS:*Yes, this was corrected.*

REF:Page 11149, line 4. "We made regular calibrations". When did you actually do these calibrations? Please write the dates down?

ANS:*The calibrations took place on a regular basis, once every month, to verify the stability of the instrument. We do not believe that the exact dates provide any further useful information. Instead we changed the corresponding sentence to:*

"Calibrations by using laboratory-generated ammonium sulfate particles of different sizes, following the procedure of Moore and Nenes (2009), were performed once every month, to verify the stability of the system."

REF:Chapter 2.3.

Page 11149. I never worked with scanning flow rate of CCNc: Is there a problem with double charged particles from the DMA in the CCN/CN versus flow rate curve when obtaining critical flow Q50? Could be worth mentioning if double charges sometimes play a role. One example is Snider et al., 2010: JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 115, D11205, doi:10.1029/2009JD012618, 2010.

ANS:*This is a good point. The size distribution of the calibration aerosol was sufficiently small so that the multiply-charged particles was a distinct secondary activation peak – which could* *subsequently omitted from the analysis. This is also stated in Moore and Nenes (2009): " The contribution of doubly charged particles and the DMA transfer function width were neglected, as this introduces negligible uncertainty in the determination of Q_{50} for the aerosol size range and the sheath-to-aerosol ratios examined.".*

REF:Page 11150. About ME-2 and PMF. I associate PMF with a specific factor analytical tool. I think of ME-2 also as a specific factor analytical tool, but different from the PMF tool. Hence, I would recommend not to refer to your method as PMF, but rather as ME-2 throughout the paper (not only this chapter), and skip writing about PMF at all.

ANS:*In the literature there are several algorithms to solve the PMF algorithm, most commonly used are the PMF2 and ME-2. We refer to the PMF as the general source apportionment algorithm and the ME-2 as the solver used.*

REF:Chapter 3.1.

Page 11153, lines 10-12. Please indicate that this parameterization for the CCN vs N100 is valid for the NPF periods.

ANS:*We modified the last two sentences of this paragraph into the following form, also correcting a typo in the formula, $CCN_{0.2}=a*N_{100}+b$ in the revised version:*

"Overall, these data suggest that during active NPF periods, particles larger than about 100 nm in diameter were able to act effectively as CCN at 0.2% supersaturation in the measured air masses, which is in line with observations made elsewhere (see Kerminen et al., 2012); we therefore recommend N_{100} as a proxy for CCN0.2 at Finokalia with a linear correction in a form $CCN_{0.2}=a*N_{100}+b$, where a and b are the slope and offset determined from our observations. For the dataset considered here, a= 0.57 ± 0.01 and b = 180 ± 9 cm^{-3}, where ± represents the standard error of these quantities with respect to the linear fit for all the data in Fig. 4."

REF:Figure 10. The labels for the different colors are missing.

ANS:*We added the missing legend.*

REF:Conclusions:

It is very important that you mention how often you have such regional new particle formation events, which can give high CCN production. Your referenced papers from Finokalia station clearly show that these kind of strong CCN-producing new particle formation events do not happen very often each year as compared to continental events. Please write how often and write a discussion about this. Otherwise, a reader, which only reads the abstract and conclusions might get the impression that these type of strong events happen very frequently during the year.

ANS:*This is an excellent point. In response to this comment, we modified the beginning of the "Conclusions" as follows:*

"Atmospheric new particle formation (NPF) is a common phenomenon over the Eastern Mediterranean atmosphere, the observed frequency of NPF event days being close to 30% at Finokalia in Crete. However, there is practically no information whether particles formed in this environment are capable of producing new CCN and how effective this pathway is. The case study presented in this paper…"

<u>References</u>

Moore, R. H. and Nenes, A.: Scanning Flow CCN Analysis - A Method for Fast Measurements of CCN Spectra, Aerosol Sci. Tech., 43, 1192–1207, doi:10.1080/02786820903289780, 2009.

Sciare, J., Oikonomou, K., Cachier, H., Mihalopoulos, N., Andreae, M.O., Maenhaut, W., and Sarda-Esteve, R.: Aerosol mass closure and reconstruction of the light scattering coefficient over the Eastern Mediterranean Sea during the MINOS campaign, Atmos. Chem. Phys. 5, 2253–2265, doi:10.5194/acp-5-2253-2005, 2005.

Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., and Baltensperger, U.: Absorption of light by soot particles: determination of the absorption coefficient by means of aethalometers, J. Aerosol Sci., 34, 1445–1463, doi:10.1016/S0021-8502(03)00359-8, 2003.

Atmospheric new-particle formation as source of CCN in the Eastern Mediterranean marine boundary layer

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Abstract

While Cloud Condensation Nuclei (CCN) production associated with atmospheric new particle formation (NPF) is thought to be frequent throughout the continental boundary layers, few studies on this phenomenon in marine air exist. Here, based on simultaneous measurement of particle number size distributions, CCN properties and aerosol chemical composition, we present the first direct evidence on CCN production resulting from NPF in the Eastern Mediterranean atmosphere. We show that condensation of both gaseous sulfuric acid and organic compounds from multiple sources leads to the rapid growth of nucleated particles to CCN sizes in this environment during the summertime. Sub-100 nm particles were found to be substantially less hygroscopic than larger particles during the period with active NPF and growth (the value of κ was lower by 0.2–0.4 for 60 nm particles compared with 120 nm particles), probably due to enrichment of organic material in the sub-100nm size range. The aerosol hygroscopicity tended to be at minimum just before the noon and at maximum in afternoon, which was very likely due to the higher sulfate to organic ratios and higher degree of oxidation of the organic material during the afternoon. Simultaneously to the formation of new particles during daytime, particles formed in the previous day or even earlier were growing into the size range relevant to cloud droplet activation, and the particles formed in the atmosphere were possibly mixed with long-range transported particles.

Deleted: Sub-100 nm particles were found to be substantially less hygroscopic than larger particles during the period with active NPF and growth (0.2−0.4 lower κ between the 60 and 120 nm particles), probably due to enrichment of organic material in the sub-100 nm size range.

1. Introduction

Aerosol particles influence the Earth's radiation balance via aerosol-radiation and aerosol-cloud interactions, the latter effect constituting one of the largest uncertainties in understanding the anthropogenic climate change (IPCC, 2013). A key quantity related to aerosol-cloud interactions is the number concentration of aerosol particles able to act as cloud condensation nuclei (CCN) at water vapour supersaturation levels relevant for ambient clouds. Supersaturations in the atmospheric water clouds remain well below 10% and most frequently below 1% (Pruppacher and Klett, 1997). The probability by which an aerosol particle acts as a CCN at a given supersaturation depends primarily on its size and secondarily on its chemical composition (Dusek et al., 2006). In a population of aerosol particles, the total CCN number concentration is affected by the chemical composition and mixing state of these particles (Karydis et al., 2012; Padró et al., 2012).

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CCN are emitted directly to the atmosphere by a variety of natural and anthropogenic sources, in addition to which CCN can also be produced in the atmosphere by the growth of both primary and secondary aerosol particles (Andreae and Rosenfeld, 2008; Pierce and Adams, 2009). Model studies suggest that a large fraction of CCN in the global atmosphere originates from atmospheric new particle formation (NPF) and growth. Merikanto et al., (2009) estimated that 45% of the global low-level-cloud CCN at 0.2% supersaturation result from nucleation (ranging between 31–49%). Westervelt et al., (2014) estimated the average global increase of the boundary-layer CCN number concentration at 0.2% supersaturation due to nucleation ranging between 49 % and 78%, depending on the simulation scenario used. The fraction of nucleated particles that can grow to CCN sizes in the boundary layer is likely to have large spatial variations, ranging from <20% for 0.4% supersaturation for Southern Ocean and exceeding 60% for the tropical oceans, Antarctica, Eastern United States, Europe and North Atlantic, whereas in the vertical dimension CCN concentration generally decrease with an increasing altitude (Yu and Luo, 2009). Field studies directly investigating the connection between atmospheric NPF, subsequent particle growth and CCN production have been mostly limited to continental boundary-layer sites (see Kerminen et al., 2012, and references therein). An example of increase in CCN sized particles concentration after coastal nucleation is presented in O. Dowd, 2001 In general, however, field measurements give support for the potentially important role of NPF in CCN production, at least regionally; nucleation observed was followed by increase in CCN number concentrations.

New particle formation is frequent in the Eastern Mediterranean atmosphere (Petäjä et al. 2007, Kalivitis et al., 2008, Manninen et al., 2010, Kalivitis et al., 2012, Pikridas at al., 2012), although a bit more sparse than in other, mostly continental, European sites (Manninen et al., 2010). Few CCN measurements have been conducted in the Eastern Mediterranean (Bougiatioti et al., 2009, 2011), and no attempt exist to date to link NPF with CCN in this environment. This study will focus on the NPF-CCN link using observations of particle number size distribution, CCN and high resolution aerosol chemical composition. The specific scientific questions, we aim to address are the following: 1) does atmospheric NPF lead to the production of new CCN in the Eastern Mediterranean atmosphere, 2) what is the relative role of sulfuric acid and low-volatile organic vapors of different origin in growing nucleated particles to CCN sizes, 3) how does the hygroscopicity of particles relevant to the cloud droplet activation vary with the particle size and time of day, and 4) what implications our findings will have on quantifying the main sources of CCN in this environment.

2. Materials and methods

2.1 Measurements location

Measurements were performed between 20 August and 25 November 2012 at the atmospheric observation station of the University of Crete at Finokalia, Crete, Greece (35˚20´N, 25˚40´E, 250m a.s.l). 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 situated directly at the top of a hill over the coastline, in the north east part of the island of Crete, facing the Mediterranean Sea in the wide north sector. Air masses sampled at Finokalia represent the marine conditions of Eastern Mediterranean (Lelieveld et al., 2002), only very slightly influenced by local anthropogenic sources. The nearest major urban center in the area is Heraklion with approximately 170 000 inhabitants, located about 50 km to the west of the measurement site. A detailed description of the Finokalia station and the climatology of the area can be found in Mihalopoulos et al. (1997).

2.2 Instrumentation

The particle number size distributions were measured in the diameter range 9−848 nm using a custom-built Scanning Mobility Particle Sizer (SMPS). The system is closed-loop, with a 5:1 ratio between the aerosol and sheath flow, it consists of a Kr-85 aerosol neutralizer (TSI 3077), a Hauke medium Differential Mobility Analyzer (DMA) and aTSI-3772 Condensation Particle Counter (CPC), and it is operated following the recommendations by Wiedensohler et al.(2012). 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 diffusional particle losses.

The chemical composition of the non-refractive mass of submicron particles was specified with an Aerodyne Research Aerosol Chemical Speciation Monitor (ACSM ; Ng et al., 2011). The ACSM provides real-time (30-min time interval) information on ammonium, sulfate, nitrate, chloride and organic mass in non-refractory submicron particles. More details and calculations of the mass concentrations can be found in Bougiatioti et al. (2014). During our measurements, the ambient air was drawn into the ACSM via a PM_1 aerosol inlet without sample drying. The concentration of black carbon (BC) was measured using an AE31 Aethalometer (Magee Scientific, AE31) operated with a PM_{10} sampling head and under humidity controlled conditions.

Aethalometer data were corrected using the empirical formula given by Weingartner et al. (2003). In this formula (their equation 4), the calibration constant *C* has been calculated to be 2.48 for the Finokalia station in summer and *R*(ATN) was taken as 1, the value representative for aged particles at remote locations (Sciare et al., 2008).

In order to investigate size-segregated CCN properties, we utilized a coupled DMA-CCNc set-up. The sampled polydisperse aerosol were driven through a TSI 3080 DMA after being charged by a Kr-85 aerosol neutralizer (TSI 3077). The DMA had a closed-loop system for recirculating the sheath flow. The monodisperse aerosol, classified at the 60, 80, 100 and 120 nm diameters out of the DMA, were then supplied to a Continuous Flow Streamwise Thermal Gradient CCN Chamber (CFSTGC; Roberts and Nenes, 2005) in order to determine the number concentration of aerosol particle able to act as CCN with respect to supersaturation. The CFSTGC was operated in the “Scanning Flow CCN Analysis” (SFCA) mode (Moore and Nenes, 2009), in which the flow rate in the CCN instrument is ranged over 1-2 minute cycles while maintaining the temperature gradient constant, which allows supersaturation to change during a flow cycle and results in a CCN spectrum every 1-2 minutes. In this study, the flow rate was varied linearly between 300 and 1000 cm^{-3} min^{-1}. Calibrations by using laboratory-generated ammonium sulfate particles of different sizes, following the procedure of Moore and Nenes (2009), were performed once every month, to verify the stability of the system. The calibration curves relating the supersaturation to the flow rate were calculated based on Köhler Theory. The absolute uncertainty of the calibrated CCNc supersaturation has been estimated to be ±0.04% (Moore et al., 2012). The total number concentration of particles (CN) was measured after the DMA. During the periods when the DMA was inoperative, the CCNc was operated at the total CCN mode where the CCN number concentration was monitored at a fixed supersaturation of 0.2%, using similar settings to Bougiatioti et al., (2009). During the study period concentrated in this paper (28 August to 2 September 2012), size-segregated CCN measurements were not available after 22:55 on 30 August, and the total CCN concentration measurements at the 0.2% supersaturation initiated at 23:15 on 1 September.

2.3 Data analysis

The CCN activation potential of the classified aerosol can be characterized with the help of the Activation Fraction (AF) defined as the CCN/CN ratio. By plotting the AF as a function of flow rate of CCNc, and thus as a function of supersaturation, the result can be fitted to a sigmoidal curve (Bougiatioti et al., 2011), where the maximum AF at the highest supersaturation measured

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is the asymptote of the curve. An example of a sigmoid activation curve is shown in Fig. 1. The flow rate Q_{50} describes the inflection point of the sigmoidal curve and corresponds to the critical supersaturation, S_c, above which particles act as CCN (Moore and Nenes, 2009). Once the value of S_c has been obtained, the hygroscopic parameter kappa (κ), can be calculated from Köhler theory using the single parameter approach of Petters and Kreidenweis (2007):

$$\kappa = \frac{4A^3}{27{D_d}^3 s_c^2}, A = \frac{4M_w\sigma_w}{RT\rho_w},$$

where M_w is the molar mass of water, σ_w is the surface tension of water, R is the universal gas constant, T is temperature, ρ_w is the density of water and D_d is the particle dry diameter. The value of κ is 0 for non-hygroscopic material and lies typically in the range 0.01−0.5 for slightly-to-highly hygroscopic organic compounds and in the range 0.5−1.5 for hygroscopic inorganic compounds (Petters and Kreidenweis, 2007).

We divided the organic mass measured with the ACSM into a few separate components using the positive matrix factorization (PMF) analysis (Paatero, 1999). For this purpose, we utilized the multi-linear solver ME-2 using the interface described by Canonaco et al. (2013). The estimated oxygen-to-carbon ratios (O/C) of the organic material were calculated following the approach by Aiken et al. (2008). Atomic O/C ratios characterize the oxidation state of organic aerosol which correlates to their density and water solubility. It has been shown that κ generally increases with the organic oxidation level (eg. Massoli et al., 2010; Mei et al., 2013)., however it should be noticed that several other studies have shown that the link between hygroscopicity and oxidation level is not straightforward (Cerully et al. 2014 and references therein)

We determined the particle growth rate (GR) during the new-particle formation events along with the condensation sink (CS), using the approach described in detail by Kulmala et al. (2012). The values of GR discussed later in this paper refer to the particle growth rates of 9−20 nm diameter particles averaged over each NPF event.

3. Results

We chose 28 August to 2 September, 2012 as our case study period, since during that time several NPF events were observed at the Finokalia station as shown in the size distributions in Fig. 2. For three consecutive days (29−31 August), NPF formation was observed before noon at the lowest detectable sizes, with subsequent growth of the newly-formed particles over the rest of the day

(Fig. 2). These days are typical examples of so-called regional NPF events, in which the particle formation and growth takes almost homogeneously place over distances of tens to hundreds of kilometers (Kulmala et al., 2012). During this time period, a low pressure system moved over the north of the Balkan Peninsula heading eastwards, and as a result the air mass origin shifted from W/NW to N/NE from the island of Crete. Four-day air mass back-trajectories calculated using the HYSPLIT model (Draxler and Hess, 1998) showed that the air masses leading to NPF during these three days originated from the free troposphere and then descended to the marine boundary layer approximately 5, 9 and 12 hours, respectively, prior to the initiation of the events (Fig. 3). A decline of air from higher altitudes into the marine boundary layer prior to NPF at Finokalia has been reported in the past as well (Kalivitis et al., 2012). It is worth noting that the back trajectories during the previous days did not show such an air mass descend. Satellite images showed broken to overcast cloud conditions over Black Sea on 28 August, quickly evaporating the following day. No significant change in the origin of the air masses during the three events on 29−31 September was observed, so in the following analysis our main focus will be on these three days.

The first (28 August) and fifth (1 September) of the events showed clear signs of the particle growth up to several tens of nm, but the newly-formed particles were not observed until they had already reached sizes larger than 20−30 nm. During these two days, NPF apparently did not take place in the immediate vicinity of the station but had rather been initiated at least a few hours before the air masses entered our measurement site. During the night between 1 and 2 September, a NPF event was observed with no apparent growth of the particles beyond the nucleation mode. Nighttime NPF events with very limited growth are relatively common in Finokalia, and such events tend to be associated with air mass transport over the island of Crete (Kalivitis et al., 2012). These features point toward the local origin of such events, so in the following analysis we will not consider the nighttime event any further.

3.1 Aerosol growth and CCN production

A key quantity in estimating the CCN production associated with atmospheric nucleation is the particle growth rate, GR, since it determines the time lag between nucleation and subsequent CCN production, and affects the fraction of nucleated particles that eventually reach CCN sizes before being lost by coagulation scavenging or other removal processes (e.g. Kerminen et al., 2012; Westervelt et al., 2014). The observed values of GR on 29, 30 and 31 August were 3.3, 1.8 and 3.6 nm h^{-1}, respectively, which are lower than the annually-averaged (±STD) GR of 5.2 ±3.4 nm h^{-1} reported by Pikridas et al.(2012) at the same site for the 10-25 nm size range. By following the approach of Laakso et al. (2013), we could follow the growth of newly-formed particles up to about 50−60 nm in particle diameter until another NPF occurred or the particle growth was interrupted by an air mass or cloud cover change. These features are suggestive of the convolution of nucleation with condensational growth of both new and preexisting particles formed in the previous day (or even earlier) to produce CCN size range particles.

When no CCN measurements are available, a commonly-used proxy for the CCN number concentration is the total number concentration of particles larger than some threshold diameter, *D*, denoted as N_D (Paasonen et al., 2013, Laakso et al., 2013). Just prior to the nucleation event period (28 August − 2 September) and after it, our CCN counter was offline the DMA due to technical problems, so that it was recording the total CCN number concentration at 0.2% supersaturation, $CCN_{0.2}$. The measured values of $CCN_{0.2}$ correlated strongly with N_{90}, N_{100}, N_{110}, N_{120} and N_{130} (Fig. 4) when considering all the available data. The relation between $CCN_{0.2}$ and N_D prior to the three-day period with most active new particle formation and growth differed greatly from the corresponding relation after this period. Prior to the NPF events (Fig. 4a), the best correlation against $CCN_{0.2}$ was observed for N_{90}, but this quantity overestimated heavily the CCN concentration (R^2=0.95, slope = 1.73). With increasing diameters, D, the value of R^2 decreased as did also the slope, so that between N_{130} and $CCN_{0.2}$ the weakest correlation and smaller slope was observed (R^2=0.78, slope = 1.17). On the other hand, after the NPF events (Fig. 4b) the picture was different: for N_{90} the correlation with $CCN_{0.2}$ was still very good (R^2=0.94, slope = 1.43), for diameters larger than 110 nm this slope dropped below 0.45, and for particles larger than 120 or 130 nm there was practically no correlation between N and $CCN_{0.2}$. The slope of the above regression analysis probably reflects the activation fraction for each diameter while R^2 values indicate that, especially in active NPF periods, the variability of CCN number may be controlled by sub-100 nm particle population. Overall, these data suggest that during active NPF periods, particles larger than about 100 nm in diameter were able to act effectively as CCN at 0.2% supersaturation in the measured air masses, which is in line with observations made elsewhere (see Kerminen et al., 2012); we therefore recommend N_{100} as a proxy for $CCN_{0.2}$ at Finokalia with a linear correction in a form $CCN_{0.2}$=a*N_{100}+b, where a and b are the slope and offset determined from our observations. For the dataset considered here, a= 0.57 ± 0.01 and b =

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180 ± 9 cm−3, where ± represents the standard error with respect to the linear fit for all the data in Fig. 4.

Next, we will examine the time evolution of the CCN proxies during our case study period (Fig. 5). We may see that the increase in the total particle number concentration, N_{tot}, caused by nucleation was often followed by an increase in N_{50} after some time lag, as one would expect due to the gradual growth of newly-formed particles up to 50 nm during the same day. The time evolution of both N_{100} and N_{130} resembled that of N_{50}, but with the difference that the base levels of N_{100} and N_{130} tended to increase gradually over time after 29 August. This latter feature supports our earlier speculation that CCN production was a multi-day process in measured air masses, at least when it comes to the CCN that are active at low supersaturations between about 0.1 and 0.3%. It should be noted that the origin of the new CCN was not necessarily only atmospheric nucleation, but also the growth of sub-CCN-size primary particles during their transportation. The apparent co-variation of N_{50}, N_{100} and N_{130} reveals that, besides new-particle formation and growth, the measured air masses had been affected to variable extents by i) dilution due to the free-troposphere entrainment, and ii) long-range-transported primary aerosol particles.

3.2 Aerosol chemical composition, hygroscopicity and CCN activity

To obtain a comprehensive understanding on particle CCN activity properties, we quantified the link between aerosol chemical composition and hygroscopicity. Fig. 6 shows that the composition of submicron particulate matter was dominated by organic material (average concentration 1.9±0.9 μg m^{-3}) and sulfate including associated ammonium (1.8±0.8 μg m^{-3}) during our case study period, while nitrate and black carbon contributed a minor fraction of the aerosol (average concentration 0.13±0.08 and 0.34±0.15μg m^{-3} respectively). Long-term measurements at Finokalia are in line with this pattern (eg Lelieveld et al., 2002; Bougiatioti et al., 2013), suggesting that the relative abundances of sulfate and organic matter dictate to large extent the hygroscopic and cloud activating properties of submicron particles at Finokalia.

In a broader picture, when averaged for the period 1 August to30 September, the aerosol chemical composition displayed a clear diurnal pattern (Fig. 7a). In general, sulfate concentrations started to increase very rapidly around the noon and reached their diurnal maximum during afternoon, after which they decreased first gradually and then more rapidly until the following noon. The afternoon increase in the sulphate concentration can be ascribed to the intensive photochemical production of gaseous sulphuric acid from both natural and anthropogenic precursors during

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daytime, followed by the condensation of sulphuric acid into pre-existing aerosol particles together with gaseous ammonia (e.g. Zerefos et al., 2000; Kouvarakis and Mihalopoulos, 2002; Bardouki et al., 2003; Mihalopoulos et al., 2007). Since sulphate is practically non-volatile, the decreasing sulphate concentrations during night and morning hours are most likely a combination of air mass dilution by entrainment and aerosol deposition processes. Organic material declined less rapidly than sulfate during morning, suggesting that secondary organic aerosol (SOA) formation was very active already before noon or, alternatively, that the organic material was less sensitive to dilution than sulfate, i.e. the concentration gradient between the mixed layer and air above it was smaller for organic material than sulphate. After noon, organic material did not increase as rapidly as sulfate, which might be either due to different photochemical pathways for sulphate and SOA formation (see e.g., Ehn et al., 2014), or due to less effective partitioning of semi-volatile organic compounds into aerosol particles at high temperatures during afternoon. Except of 28 August, the sky was cloud-free during our study period. Compared with the whole August−September period, the diurnal cycles of suphate and organic material during our case study period (Fig. 7b) were similar, even though less pronounced.

The diurnal variability in the aerosol chemical composition was reflected in the hygroscopic properties of particles at sizes critical to the cloud droplet activation (<150 nm). In Fig.8a the daily variation of the hygroscopicity (κ parameter) of 60−120 nm particles averaged over two full days is presented and in Fig. 8b the corresponding normalized values to the average κ of each diameter. As we may see, κ tended to decrease quite rapidly during early morning hours in our case study period, presumably due to the production of SOA of relatively low hygroscopicity. At some point around noon, the hygroscopicity of 80−120 nm particles started to increase again, as one would expect due to the formation of particulate sulphate at this time of the day. Smaller particles were much less hygroscopic than larger ones, the difference being 0.2−0.4 κ units between the 60 and 120 nm particles. A similar decrease in the value of κ when going below 100 nm in particle diameter has been reported in a few other field studies (Dusek et al., 2010; Cerully et al., 2011; Levin et al., 2012; Paramonov et al., 2013; Liu et al., 2014). This feature has been ascribed to the enrichment of organic material in sub-100 nm particles, combined with the usually more aged character of accumulation mode particles compared with sub-100 nm particles. Unfortunately, we had no size-resolved chemical aerosol measurements in our study period to look into this issue in more detail.

In addition to the relative amounts of sulfate to organic material, the character of the organic material influences aerosol hygroscopic properties (e.g. Chang et al., 2010; Moore et al., 2012;

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Kuwata et al., 2013; Cerully et al., 2014) although the link is tenuous or highly variable. By making a PMF analysis for the organic material measured by the ACSM, we found three major contributing factors: the factor OOA representing oxygenated organic aerosol, the factor OOA-BB that can be classified as processed biomass-burning organic aerosol, and the factor that resembles the SOA from α-pinene oxidation. Representative mass spectra of the first two of these factors can be found in Bougiatioti et al. (2014) and of the last one in Bahreini et al. (2005). During our case study period (Fig. 9), OOA explained the largest fraction of the total organic mass (average 46%), followed by OOA-BB (38%) and α-pinene SOA (16%). The high fraction of OOA-BB can be ascribed to the measured air masses being affected by forest fires in Croatia (Bougiatioti et al., 2014). The OOA observed at Finokalia during summer have multiple possible sources, including also aged biomass burning aerosol (Hildebrandt et al., 2010; Bougiatioti et al., 2014). The α-pinene SOA, while evident during our case study period when active NPF and growth was taking place, did not stand out during the rest of August−September, 2012. The O/C ratio of the organic material was close to or above unity during our case study period (Fig. 9), indicating that most of the organic compounds in aerosol particles were highly oxidized (see, e.g. Chang et al., 2010; Kuwata et al., 2013). The highest values of O/C were observed in the afternoon when the photochemical activity is at its highest, consistent with earlier findings at Finokalia (Hildebrandt et al., 2010). Since the SOA originating from the oxidation of α-pinene and many other terpenes is only slightly hygroscopic (e.g. Duplissy et al. 2008, Engelhart et al., 2011; Alfarra et al., 2013), its abundance before noon very likely contributed to the low κ values observed during that time of the day.

Finally, we investigated the mixing state of particles at sizes critical to CCN activation. The maximum values of AF remained above 0.8 for 80−120 nm particles, indicating that particles in this size range did not show a high degree of external mixture during our case study period (Fig. 10). Contrary to this, the maximum value of AF for 60 nm particles decreased substantially on 29 and 30 August (Fig. 10a). Interestingly, this decrease started approximately at the time when particles nucleated in the previous day had reached 60 nm as a result of their growth as can be seen in Fig. 10b that the average diurnal cycle of AF for these two days is presented. It therefore seems that there were two types of 60 nm particles during our case study period: those formed by recent atmospheric nucleation (less hygroscopic) and those that were more aged (more hygroscopic) ones. The origin of the latter particle type, whether nucleation or primary emissions, remains unsolved. A similar observation has been reported for 40 nm particles by Cerully et al., (2011) in a boreal forest, attributing the low AF to not reaching the asymptote of the sigmoidal

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curve at the highest supersaturation measured for 40 nm spectra. The AF for 40 nm particles did not reach nevertheless as low AF as the ones shown in Fig.10 for 60 nm particles.

3.3 Implications for cloud droplet activation

Fig. 11 summarizes the cloud activating properties of 60, 80, 100 and 120 nm diameter particles during 29−30 August, 2012, the two days with a pronounced new particle formation and growth in our case study period. There are several things to be noted. First, the supersaturation required for cloud droplet activation increased more steeply with decreasing particle size than it would do if all the particles were equally hygroscopic. A similar feature has been observed in a few earlier studies (Levin et al., 2012; Paramonov et al., 2013; Liu et al., 2014), and it has generally been ascribed to the enrichment of organic material in ultrafine (<100 nm) particles. The main implication of this finding is that ultrafine particles tend to need higher cloud supersaturations to be able to act as CCN than one would expect based on the bulk chemical composition of the submicron particulate matter. Second, the hygroscopicity of 60−120 nm particles showed a clear diurnal cycle, with the minimum and maximum values of κ typically observed just before and after noon, respectively (Fig. 8). As discussed earlier, this feature was very likely due to higher sulfate to organic ratios (Fig. 7) and higher degree of oxidation of the organic material (Fig. 9) after noon. Fig. 7b suggests that the notable diurnal variability in the efficiency by which different-size particles act as CCN may be a common feature at Finokalia during summer. Finally, the required supersaturation needed for CCN activation varied easily by more than a factor 2 for given particle size even at the same time of the day, while the corresponding variability in the smallest diameter of particles able to act CCN at given cloud supersaturation was 20−30 nm.

The maximum supersaturation remains usually below 0.3% in polluted boundary layer clouds, while higher supersaturations close to or even larger than 1% have been reported under clean conditions and in convective clouds (Ditas et al., 2012; Hammer et al., 2014; Hudson and Noble, 2014). As discussed in Sect. 3.1, we were able to follow the growth of nucleated particles up to 50−60 nm in air masses measured in Finokalia during our case study period. Such particles would probably contribute little to the population of cloud droplets around Finokalia. However, we also found that the nuclei growth very likely continued to larger sizes, but at this point nucleated particles could not be separated from aged primary particles with the available measurements. We conclude that aerosol nucleation taking place in the Eastern Mediterranean environment is capable of producing new CCN at cloud supersaturations encountered in this environment.

4. Conclusions

Atmospheric new particle formation (NPF) is a common phenomenon over the Eastern Mediterranean atmosphere, the observed frequency of NPF event days being close to 30% at Finokalia in Crete. However, there is practically no information whether particles formed in this environment are capable of producing new CCN and how effective this pathway is. The case study presented in this paper provides, for the first time, direct evidence on CCN production associated with atmospheric NPF and growth in the Eastern Mediterranean atmosphere. We found that, simultaneous with the formation of new particles during daytime, particles formed in the previous day or even earlier were growing into the size range relevant to cloud droplet activation, and that particles formed originally in the atmosphere were possibly mixed with long-range transported primary particles in the measured air masses. The complicated connection between primary and secondary CCN suggests it will be very difficult to close the regional CCN budget in terms of the most important CCN sources in this environment.

Aerosol chemical measurements suggest that both gaseous sulfuric acid and organic compounds play important roles in growing nucleated particles to CCN sizes over the Eastern Mediterranean during summertime. The organic compounds contributing to the nuclei growth appear to have multiple sources at this time of the year, including biogenic emissions, biomass burning and possibly other anthropogenic sources of distant origin. The hygroscopicity of particles critical to the cloud droplet activation (<150 nm diameter) were found to vary with both particle size and time of day. Small particles were substantially less hygroscopic than larger ones, probably due to enrichment of organic material in the sub-100 nm particles. Particles larger than 100 nm in diameter may be used as a proxy for CCN in the area. The aerosol hygroscopicity tended to be at minimum just before the noon and at maximum at some time in afternoon, which was very likely due to the higher sulfate to organic ratios and higher degree of oxidation of the organic material during afternoon. The diversity in the hygroscopic properties of sub-150 nm particles is clearly an issue requiring further attention.

This case study has demonstrated the power of simultaneous particle number size distribution, CCN and aerosols chemical measurements in investigating the origin of CCN in a polluted marine environment, as well as their limitations in distinguishing sources and sinks. Understanding and quantification of the contribution of NPF to the CCN budget over Eastern Mediterranean would require comprehensive observations at extended time periods in this environment complemented with regional-scale aerosol dynamical model simulations.. Such measurements should include not only those applied here but also near-real time measurements of the size-resolved chemical composition of ultrafine (<100 nm) particles, gas-phase compounds responsible for the nuclei growth (sulphuric acid and extremely low-volatile organic compounds(see Ehn et al., 2014), potential precursors for low-volatile vapours (e.g. terpenes and organic compounds associated with biomass burning, see Vakkari et al., 2014), as well as the concentrations and size distributions of small (<3−10 nm) neutral and charged clusters. Interpretation of such measurements would benefit from some information on the diurnal evolution of the atmospheric boundary layer, volatility distributions as well as from both regional and smaller-scale modeling of aerosol-trace gas interactions in this environment.

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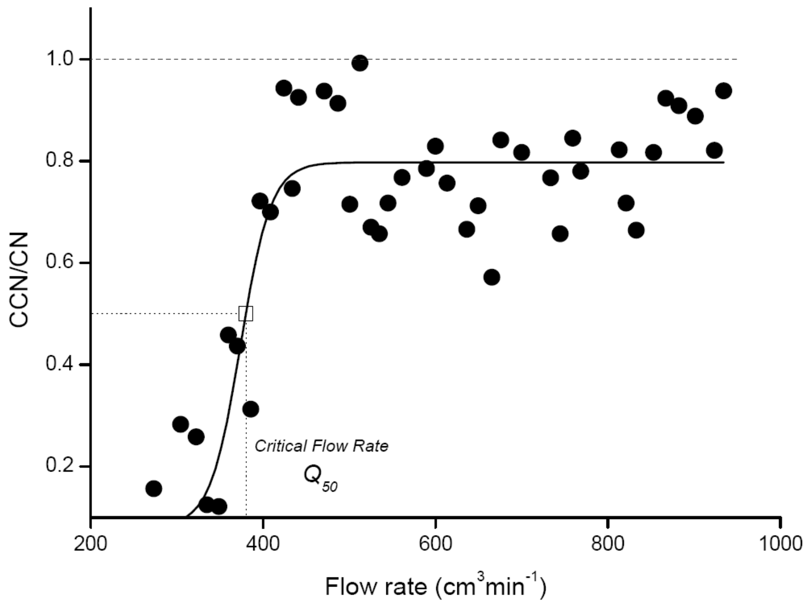

Fig1. Example of an ambient CCN activity spectrum (at a constant temperature difference) with a sigmoidal fit and the associated critical flow Q_{50}.

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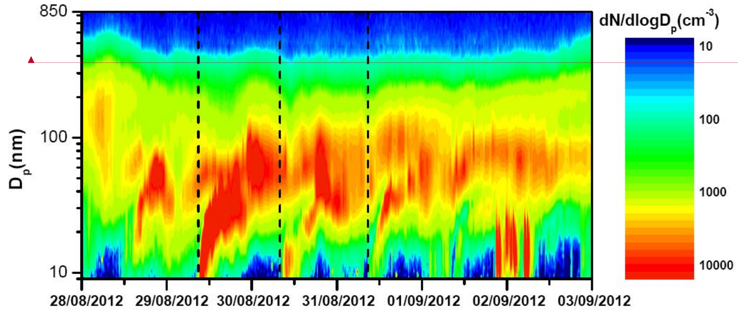

Fig. 2. Time evolution of the particle number size distribution over the diameter range 9–848 nm between 28 August and 2 September, 2012, a period of active new particle formation observed at Finokalia. The dashed vertical lines in the figure indicate the times when newly formed particles started to appear to the measured size spectra during the three NPF events concentrated in our analysis.

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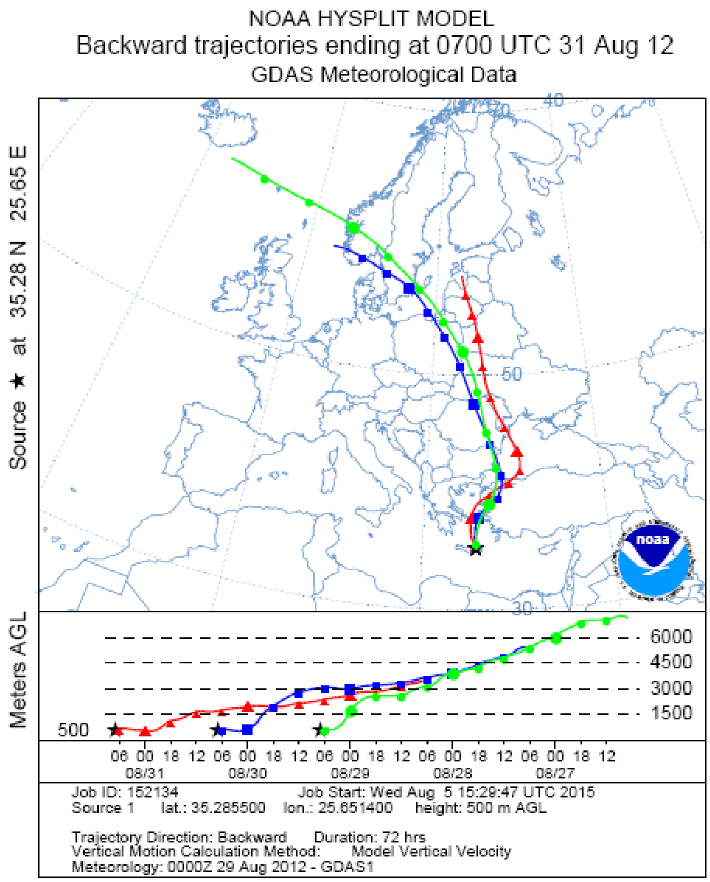

Fig. 3 Three-day back trajectories for air masses arriving at Finokalia on 29, 30 and 31 August, 2012.

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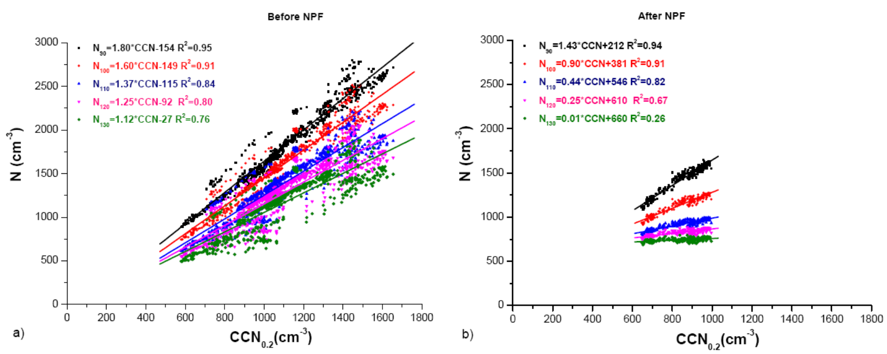

Fig. 4. Relation between the total number concentration of particles with diameter larger than D, N_D, (D = 90, 100, 110, 120 or 130 nm) and measured CCN number concentration at the supersaturation of 0.2 %. The data are from two periods in 2012: from 25 August at 23:05 to 28 August at 10:45 (panel a) and from 1 September at 23:15 to 2 September at 17:15 UTC+2 (panel b).

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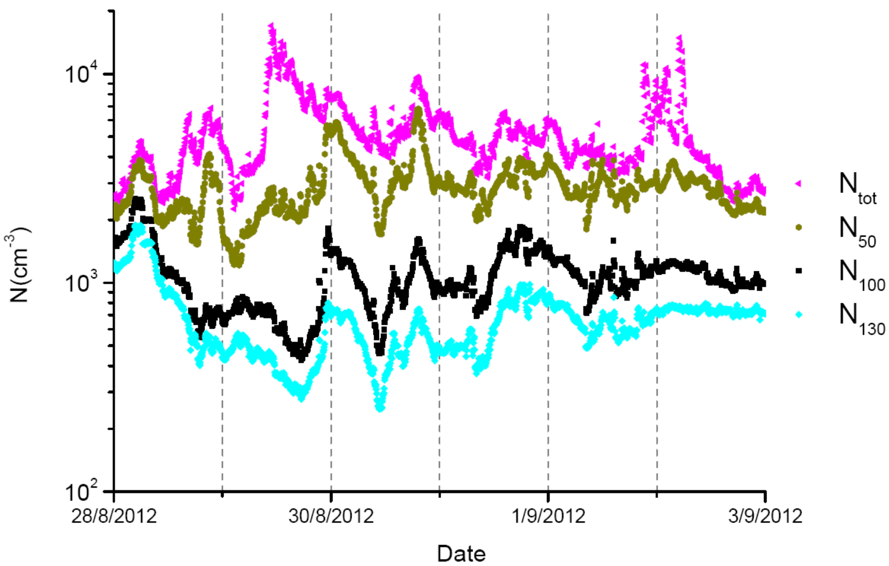

Fig. 5. Time evolution of the total particle number concentration (N_{tot}) along with N_{50}, N_{100} and N_{130} during the period 28 August – 2 September, 2012.

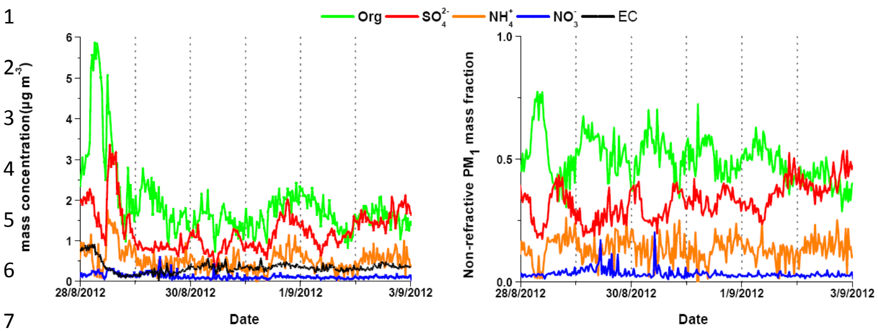

Fig. 6. Time evolution of the aerosol chemical composition during the period 28 August – 2 September 2012. Left panel: absolute concentrations (µg m^{-3}) in the PM_1 fraction of the measured aerosol, except for EC which was measured in the PM_{10} fraction . Right panel: relative contributions to the non-refractive PM_1 mass.

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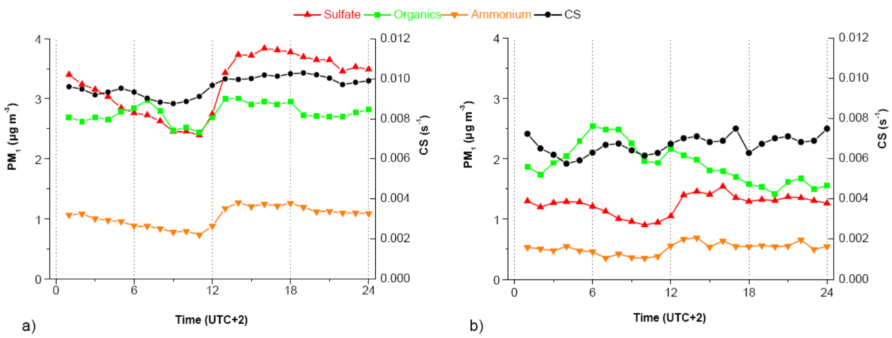

Fig. 7. Diurnal concentration cycles of sulfate, ammonium and organic material in sub-micron aerosols, as well as the diurnal cycle of condensation sink, CS, averaged over the 1 August-30 September period (a) and over the period 28 August – 2 September (b) in 2012.

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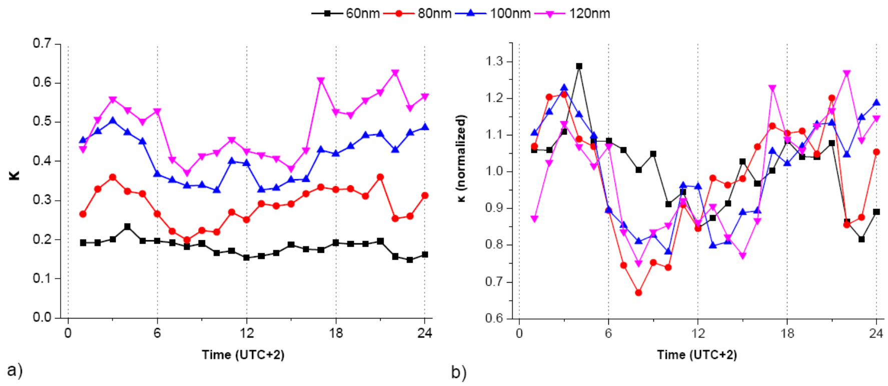

Fig. 8. Diurnal variability during the period from 28 August at 12:00 to 30 August at 12:00 of a) the hygrocopicity parameters κ for 60, 80, 100 and 120 nm particles and b) the corresponding values normalized to the average κ value for each diameter.

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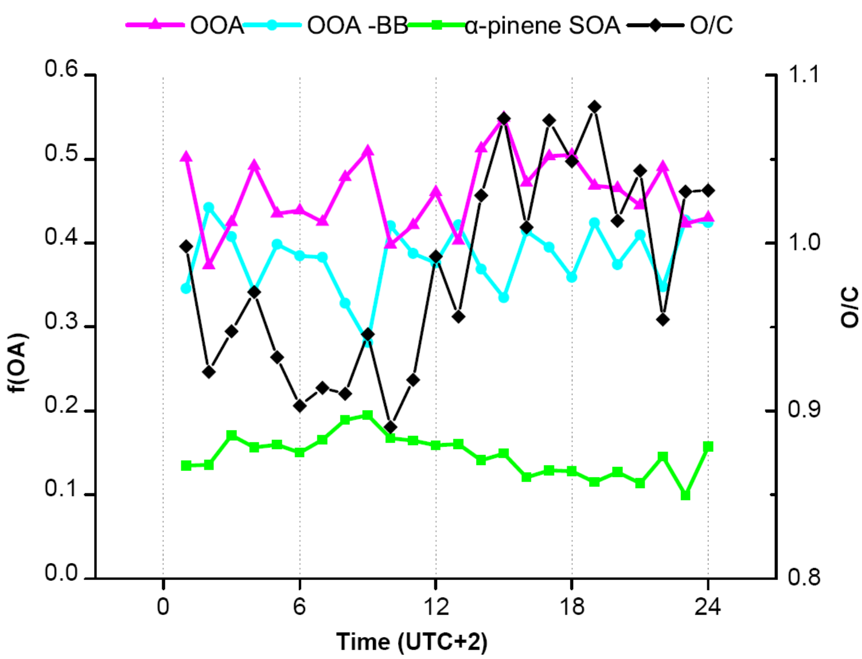

Fig. 9. Diurnal variability of the three major classes of organic aerosol obtained from the PMF analysis, along with the O/C ratio, during the period 28 August to 2 September. The quantity f(OA) represents the fractions of individual organic compounds of the total organic mass, where OA refers to OOA, OOA-BB or α-pinene SOA.

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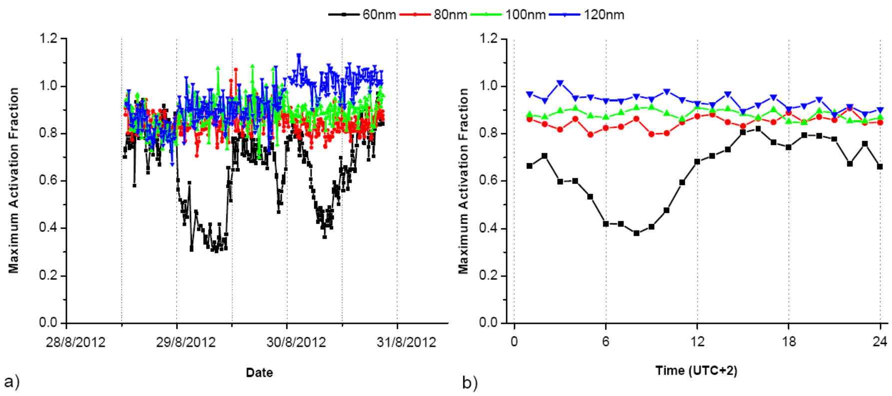

Fig. 10. a) Maximum activation fraction of 60,80, 100 and 120 nm particles between 28 and 30 August, 2012. b) Diurnal cycle of the maximum activated fraction for the same period.

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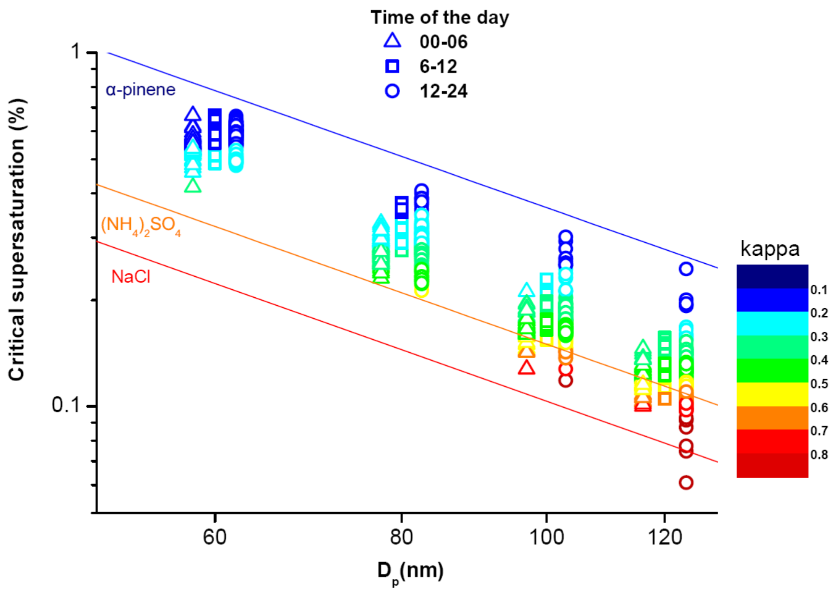

Fig. 11. Measured critical supersaturations of 60, 80, 100 and 120 nm diameter particles during different times of the day on 28 and 30 August, 2012. The color scale indicates different values of the particle hygroscopicity parameter, *κ*. Also, theoretical curves for α-pinene, ammonium sulfate and sodium chloride.

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