New particle formation at a remote site in the eastern Mediterranean

Michael Pikridas,[1,2] Ilona Riipinen,[1,3] Lea Hildebrandt,[3] Evangelia Kostenidou,[1,2] Hanna Manninen,[4] Nikos Mihalopoulos,[5] Nikos Kalivitis,[5] John F. Burkhart,[6] Andreas Stohl,[6] Markku Kulmala,[4] and Spyros N. Pandis[1,2,3]

[1]   A year (6-April–2008 to 14-April–2009) of particulate monitoring was conducted at a remote coastal station on the island of Crete, Greece in the eastern Mediterranean. Fifty-eight regional new particle formation events were observed with an Air Ion Spectrometer (AIS), half of which occurred during the coldest months of the year (December–March). Particle formation was favored by air masses arriving from the west that crossed Crete or southern Greece prior to reaching the site and also by lower-than-average condensational sinks (CS). Aerosol composition data, which were acquired during month-long campaigns in the summer and winter, suggest that nucleation events occurred only when particles were neutral. This is consistent with the hypothesis that a lack of NH_3, during periods when particles are acidic, may limit nucleation in sulfate-rich environments. Nucleation was not limited by the availability of SO_2 alone, as nucleation events often did not take place during periods with high SO_2 or H_2SO_4 concentrations. The above results support the hypothesis that an additional reactant (other than H_2SO_4) plays an important role in the formation and/or growth of new particles. Our results are consistent with NH_3 being this missing reactant.

Citation: Pikridas, M., et al. (2012), New particle formation at a remote site in the eastern Mediterranean, *J. Geophys. Res.*, *117*, D12205, doi:10.1029/2012JD017570.

1.   Introduction

[2]   Formation of new particles in the atmosphere is frequently observed at many different sites around the world [*Kulmala et al.*, 2004] and is of interest due to the particles' effect on radiative forcing, cloud formation and lifetime [*Charlson and Heitzenberg*, 1995]. Even though sulfuric acid has been identified as a key component in aerosol formation and growth [*Kulmala and Laaksonen*, 1990], it is clear that other chemical compounds often participate in the formation and growth of new particles [*Kulmala et al.*, 2004]. Ammonia, amines, iodine and organics have been suggested as potential candidates in different environments

[*Ball et al.*, 1999; *Kulmala et al.*, 2002; *Jimenez et al.*, 2003; *Jung et al.*, 2008; *Benson et al.*, 2009, 2011; *Berndt et al.*, 2010; *Erupe et al.*, 2011], but due to instrumentation limitations the composition of the fresh nuclei remains unknown. The recently developed Atmospheric Pressure Interface Time-of-Flight Mass Spectrometer (APi-TOF, Tofwerk AG) can measure the chemical composition of the naturally charged fraction of ions [*Junninen et al.*, 2010] and may contribute to our understanding of the particle formation process [*Ehn et al.*, 2010].

[3]   The sulfuric acid – water binary nucleation rates [*Kulmala and Laaksonen*, 1990; *Laaksonen et al.*, 1999; *Vehkamäki et al.*, 2002] often appear to be too low to explain observed nucleation rates in the planetary boundary layer [*Weber et al.*, 1999]. Ternary nucleation theory [*Korhonen et al.*, 1999; *Kulmala et al.*, 2002; *Napari et al.* 2002; *Merikanto et al.*, 2007] includes ammonia whose presence considerably decreases the equilibrium vapor pressure of sulfuric acid above the solution surface [*Coffman and Hegg*, 1995]. Ternary nucleation theories have also been used as a basis for the development of second-generation semi-empirical parameterizations [*Jung et al.*, 2008] that try to correct the original rates that appear to be too high compared with ambient observations [*Kulmala et al.*, 2002]. According to *Jung et al.* [2006], nucleation does not occur in sulfur rich areas if there is not enough ammonia to neutralize all particulate sulfate. If sufficient NH_3 is present then nucleation ends when ammonia is consumed following the condensation

[1]Department of Chemical Engineering, University of Patras, Patras, Greece.
[2]Institute of Chemical Engineering Sciences, ICE-HT/FORTH, Patras, Greece.
[3]Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh, Pennsylvania, USA.
[4]Department of Physics, University of Helsinki, Helsinki, Finland.
[5]Department of Chemistry, University of Crete, Heraklion, Greece.
[6]Department of Atmospheric and Climate Research, Norwegian Institute for Air Research, Kjeller, Norway.

Corresponding author: S. N. Pandis, Department of Chemical Engineering, University of Patras, Karatheodoris 1, University Campus GR 265 00 Patras, Greece. (spyros@andrew.cmu.edu)

of sulfuric acid into the newly formed and pre-existing particles. This however does not reflect the composition of the stable cluster which in the same study is predicted to include two molecules of ammonia and two of sulfuric acid and hence is acidic.

[4] Ion-induced nucleation results in early cluster stabilization via condensation onto pre-existing ions and typically occurs at higher altitudes [*Lovejoy et al.*, 2004]. Observations from a variety of European sites suggest that ion-induced mechanisms are not enough to explain the observed 2 nm particle formation rates [*Manninen et al.*, 2010]. *Kulmala et al.* [2000, 2006] proposed that thermodynamically stable clusters are always present but grow only at favorable conditions. Kinetic nucleation theory assumes the formation of dimers as potential particle formation nuclei [*Lushnikov and Kulmala*, 1998]. Particle concentrations during nucleation events vary within the boundaries predicted by the cluster activation and kinetic nucleation theory at a remote site in a boreal forest [*Sihto et al.*, 2006] and in a polluted environment [*Riipinen et al.*, 2007]. Recent smog chamber experiments indicate that semi-volatile organic compounds may also be affecting the nucleation process [*Metzger et al.*, 2010]. Recent studies on the formation and composition of the smallest observable particles depict however, an important role of basic gases (such as NH_3 and amines) as cluster stabilizing agents [*Berndt et al.*, 2010; *Ehn et al.*, 2010; *Erupe et al.*, 2011].

[5] Besides the presence or absence of certain compounds, nucleation is also affected by meteorological parameters. It is a photo-induced phenomenon and mainly occurs during daytime under direct sunlight while the presence of clouds acts as an inhibitor [*Stanier et al.*, 2004; *Boy and Kulmala*, 2002]. Even though theoretical models predict that increasing relative humidity (RH) results in higher nucleation rates [*Kulmala et al.*, 2002] ambient measurements show that, indirectly, increasing RH can be a nucleation inhibitor. The surface area of existing particles increases as the ambient RH increases and high RH values are also often connected with cloudy conditions [*Vehkamäki et al.*, 2004; *Lyubovtseva et al.*, 2005].

[6] In a previous work particle formation was investigated at Finokalia (the site of our measurements) for a two month period but without monitoring particles below 18 nm [*Kalivitis et al.*, 2008]. The three nucleation events which occurred during that period took place in air masses arriving from the west and resulted in an 80–100% increase of the particle number concentration. Coastal particle formation has been investigated extensively along the Irish coastline where it is driven by low tides. The observed nucleation in Mace Head is consistent with ternary nucleation rates with IO_2 as the third constituent [*O'Dowd et al.*, 2002b; *O'Dowd and de Leeuw*, 2007]. At Bodega Bay, California, nucleation has been also associated with ocean upwelling and occurs only close to the shore. Because the phenomenon is limited in space, observed newly formed particles in the coastal site did not grow to the Aitken mode [*Wen et al.*, 2006].

[7] In this paper we test the hypothesis that a third reactant other than sulfuric acid and water is involved in new particle formation. We focus especially on the role of NH_3 which has been suggested as a potential candidate for the third reactant. We study events that occurred between April 2008 and April 2009 at a remote coastal station located in the southeast of

the Mediterranean Sea on the island of Crete, Greece, and we try to characterize them in terms of aerosol composition and seasonality. We will test the hypothesis that nucleation events at Finokalia are not limited by the sulfuric acid availability or the condensation sink but mainly by the ammonia levels. We will utilize aerosol thermodynamic theory and the available aerosol composition measurements to identify periods of practically zero (<1 ppt) gas-phase ammonia concentrations. Synthesizing these findings we will try to explain the unexpected seasonal pattern and frequency of nucleation events at the area.

2. Experimental Results

2.1. Sampling Site

[8] Measurements were conducted at the Finokalia station (35°24′ N 25°60′ E) which belongs to the network of European Supersites for Atmospheric Aerosol Research (EUSAAR). The station is located at a remote coastal site in the southeast of the Mediterranean Sea on the island of Crete, Greece at a top of a hill in the steep slope of a mountain reaching all the way to the sea. The nearest large urban center is Heraklion with 150,000 inhabitants, located 50 km west of Finokalia. No notable human activity is present at a range of approximately 15 km from the site [*Kouvarakis et al.*, 2000]. There are very few trees and little vegetation in the surrounding area. Most of the aerosol at the site is transported from the surrounding regions (Greece, Turkey, northern Africa, eastern and central Europe) [*Pikridas et al.*, 2010]. Tidal amplitudes in the Mediterranean Sea (and hence at Finokalia) are of the order of a few centimeters [*El-Geziry*, 2010].

2.2. Measurement Period

[9] Particle formation events were followed for one year (April–08 to April–09) during which two intensive campaigns took place, the Finokalia Aerosol Measurement Experiment -2008 and -2009 (FAME-08 and FAME-09), both part of the EUCAARI intensive campaigns [*Kulmala et al.*, 2009]. FAME-08 took place in the early summer (4 May to 8 June) [*Pikridas et al.*, 2010], while FAME-09 took place during the late winter (25 February to 26 March 2009) [*Hildebrandt et al.*, 2010b].

[10] The main objective of the EUCAARI field campaigns was the understanding of the interactions of climate and air pollution, and involved a number of ground monitoring sites including Finokalia. Measurements were performed at different locations in Europe from April 2008 to May 2009. FAME-08 and -09 were month-long campaigns at Finokalia that provided more extensive measurements during the summer and winter, respectively.

2.3. Instrumentation

[11] For the one year period under investigation an Air Ion Spectrometer (AIS) [*Mirme et al.*, 2007] was used to monitor air ions ranging from 0.8 to 40 nm in diameter. The AIS measures simultaneously the positive and negative ion distributions from 3.2 to 0.0013 cm^2 V^{-1} s^{-1} (approximately 0.8–40 nm diameter). The spectrometer tends to overestimate low concentrations of cluster ions. This is caused by a natural production of small ions (<1 nm, 10 to 100 cm^{-3}) inside the spectrometer. Particle number size distributions of
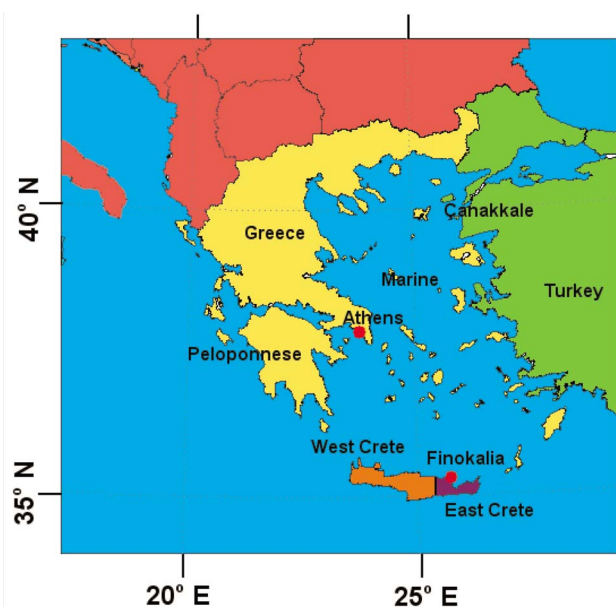
Figure 1. Source regions used in the retroplume analysis (Greece, Turkey, west Crete, east Crete and marine). The sampling station (Finokalia) and Athens (population approximately 5 million people) are also denoted on the map.

dried ambient aerosol (RH < 40%) were monitored using a custom-made Differential Mobility Particle Sizer (DMPS) [*Birmili et al.*, 1999] at a size range of 9–900 nm. The AIS measures only the naturally charged particles and therefore its measured concentrations are much lower than those of the Scanning Mobility Particle Sizer (SMPS) or DMPS for the same size range. AIS and SMPS/DMPS measurements were corrected for diffusion losses within the instruments and care was taken to minimize the diffusion losses in the sampling lines. Also meteorological parameters (RH, temperature, solar irradiance, wind speed) were monitored throughout the campaign.

[12] During the two intensive campaigns, the size distribution of aerosol at ambient relative humidity was also monitored by a SMPS (TSI model 3034 – FAME-08; TSI model 3080 – FAME-09) and the size-resolved chemical composition of ambient non-refractory particulate matter of diameter less than 1 μm (PM$_1$) was measured, without drying of the air samples, using a Quadropole – Aerosol Mass Spectrometer (Q-AMS) from Aerodyne Research, Inc. [*Jayne et al.*, 2000; *Canagaratna et al.*, 2007]. The calibration of the Q-AMS and the analysis of the spectra during both campaigns are discussed in detail by *Hildebrandt et al.* [2010a, 2010b].

[13] Ambient composition of particulate matter of diameter less than 1.3 μm (PM$_{1.3}$) was monitored using filters (Millipore, Fluoropore membrane filters of 3.0 μm pore size) with daily resolution during FAME-08 and FAME-09 and found to correlate well (R^2 = 0.95 for sulfate and 0.86 for ammonium) with Q-AMS measurements [*Pikridas et al.*, 2010]. Gaseous acidic species (SO$_2$, HNO$_3$) were monitored using alkaline impregnated filters positioned after the particulate filters with 6-h and 12-h resolution during FAME-08 and FAME-09, respectively. During both campaigns the inorganic semi-volatile (e.g., nitrates) concentrations were low

(<0.1 μg m^{-3}).The particle composition based on the filter analysis has been presented by *Pikridas et al.* [2010].

[14] For each campaign a sulfuric acid proxy was calculated based on the SO$_2$ measurements, the photolysis frequency of NO$_2$ (J$_{NO2}$) and the calculated CS. *Hildebrandt et al.* [2010a] used the photolysis frequency of NO$_2$ to estimate the concentration of the OH radical at Finokalia, based on the correlations of *Berresheim et al.* [2003]. Following the same procedure we estimated the OH radical concentration and combined it with the SO$_2$ measurements and the calculated condensational sink (see section 2.6) to estimate the sulfuric acid concentration according to:

$$[H_2SO_4] = k_{OH}\frac{[SO_2][OH]}{CS} \tag{1}$$

where k_{OH} is the reaction constant of SO$_2$ with the OH radical and is equal to 8.5×10^{-13} cm^3 molecules^{-1} s^{-1} at 298 K [*DeMore et al.*, 1997]; [OH] and [SO$_2$] are the concentrations of OH and SO$_2$, respectively and *CS* is the condensational sink. Equation (1) is based on the assumptions that the oxidation of SO$_2$ by the hydroxyl radical is the only sulfuric acid source, the major sink is the condensation of sulfuric acid onto the existing aerosol surface and the system is at pseudo-steady state. At Finokalia these assumptions are valid [*Bardouki et al.*, 2003]. These authors using an equation similar to equation (1) based on similar SO$_2$ filter measurements found very good correlation (R^2 = 0.85) of the predicted H$_2$SO$_4$ concentrations with values measured by a CIMS. This is due to the fact that the Finokalia site is remote and therefore pollutant concentrations change relatively slowly (compared to sites close to sources). Therefore, the available SO$_2$ filter based measurements for Finokalia should provide a fair estimate of sulfuric acid concentrations. The uncertainty of this approximation for the summer period is a combination of the SO$_2$ measurement uncertainty, the condensation sink estimation, and of J$_{NO2.}$ In this work we used the same methods as *Bardouki et al.* [2003], hence we expect the same overall uncertainty. However, the uncertainty of the estimated sulfuric acid levels during the winter is expected to be significantly higher because of the extrapolation from the summer to the winter and the lower temporal resolution SO$_2$ measurements.

2.4. Retroplume Analysis

[15] Following the source region approach of *Pikridas et al.* [2010] we categorized the air masses sampled at the station based on their source region using the footprint potential emission sensitivity (PES) from 20-day retroplume calculations with the particle dispersion model FLEXPART in backward mode [*Stohl et al.*, 2005], with three hour resolution. Additional information about PES calculations can be found in *Seibert and Frank* [2004]. A retroplume was attributed to a region if that region had a PES value above 0.9 ns kg^{-1}. For periods in which more than one source region had PES values above the threshold, we attributed the air mass to the region over which the retroplume passed last before reaching the site. The categories used were named by the region from which the air originated: Marine, Greece, other continental, west Crete and east Crete (Figure 1). In order to characterize a retroplume as marine, all PES values above 0.9 ns kg^{-1} had to be located over the sea.
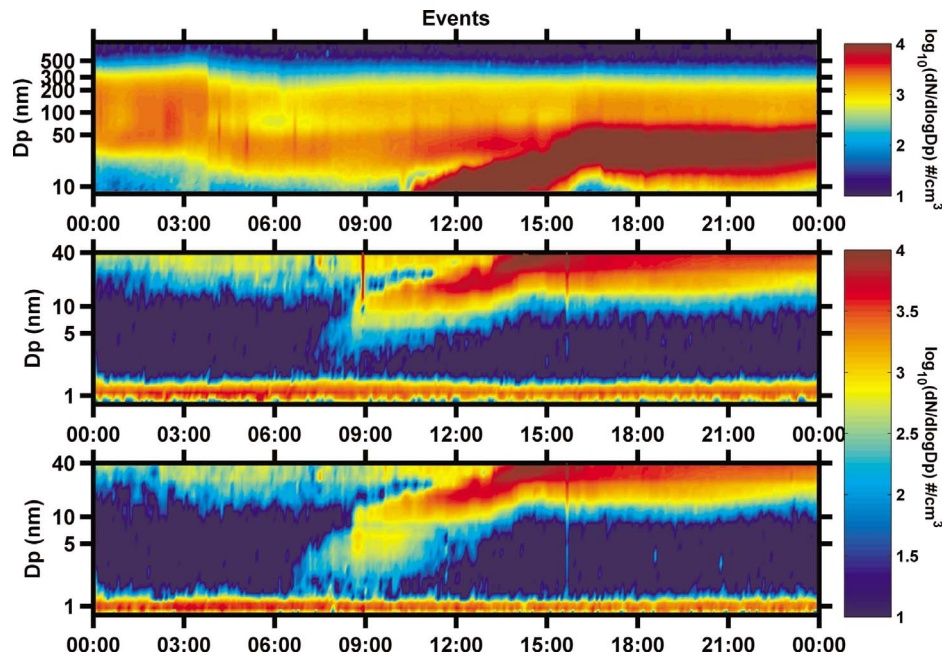
Figure 2a. SMPS and AIS measurements during a nucleation event day (19 March 2009) at Finokalia. (top) SMPS distribution ranging from 10 nm to 500 nm. (bottom) Positive and (middle) negative ion distributions ranging from 0.8 nm to 40 nm measured by an AIS. Time of day corresponds to local standard time (UTC+2).

[16] For each source region i the normalized frequency F_i of nucleation was calculated as:

$$F_i = N_{total} \frac{N_i}{N_{i,total}} \tag{2}$$

where N_i is the number of nucleation event retroplumes associated with the source region i, $N_{i,total}$ is the sum of all retroplumes associated with this source region and N_{total} is the number of retroplumes investigated regardless of source region, equal to 1046 in this study. The normalized frequency F_i corresponds to the number of nucleation events per year if the wind was always coming from the source region i.

2.5. Particle Formation Event Categorization

[17] The observation period was divided into particle formation event days, non-event days and undefined days. The data classification follows closely the work of *Manninen et al.* [2010], which combined the classification schemes introduced by *Dal Maso et al.* [2005] and *Hirsikko et al.* [2007]. In this work, however, we chose to concentrate on the regional nucleation events that show clear condensational growth (event classes I and II in *Manninen et al.* [2010]). In general, a day is classified as a regional particle formation event day if a nucleation mode is present for several hours and grows continuously during the course of the day. In this work the appearance of a nucleation mode corresponds to an increase of the charged particle concentration in the 2–10 nm range above 15 cm^{-3} for more than an hour. The concentration of charged particles in this range is typically much less than 10 cm^{-3}. If no traces of a nucleation mode are seen, a day is classified as a non-event day. Days that did not clearly belong to either of the

aforementioned categories were classified as undefined, including those during which a particle burst was picked up by the AIS without subsequent condensational growth and those during which the nucleation mode is not clear. Days during which particle formation was measured by the AIS, but not the SMPS are included in the undefined days. Some of the days regarded as "undefined" by *Manninen et al.* [2010] are in this work considered as "non-event" days.

[18] AIS positive and negative-ion along with SMPS measurements during typical event, undefined and non-event days are presented in Figures 2a, 2b and 2c, respectively. Particle formation was identified by an increase of concentration in the 2 to 10 nm range, which was less than 10 cm^{-3} on non-event days, and the subsequent growth of the freshly formed nucleation mode. Because the concentration of air ions is typically low from 2 to 10 nm, it provides a very sensitive way to follow nucleation events. This distribution of naturally charged air ions (Figure 2) is not unique at Finokalia but has been observed elsewhere [*Manninen et al.*, 2010].

2.6. Nucleation Event Characteristics

[19] *Event Duration*: In order to calculate the duration of an event, the total number concentration of air ions with diameter between 2 and 10 nm versus time was followed and fitted to a normal distribution [*Hirsikko et al.*, 2005]. The beginning and end of an event was determined by the initial increase and maximum of the total number concentration fit, respectively. Decrease of the number concentration implies that the rate of particle production is lower than the combined rates of coagulation and particle growth above 10 nm or that the air mass is getting diluted; it does not necessarily imply that the rate of production is zero. Thus, our calculated
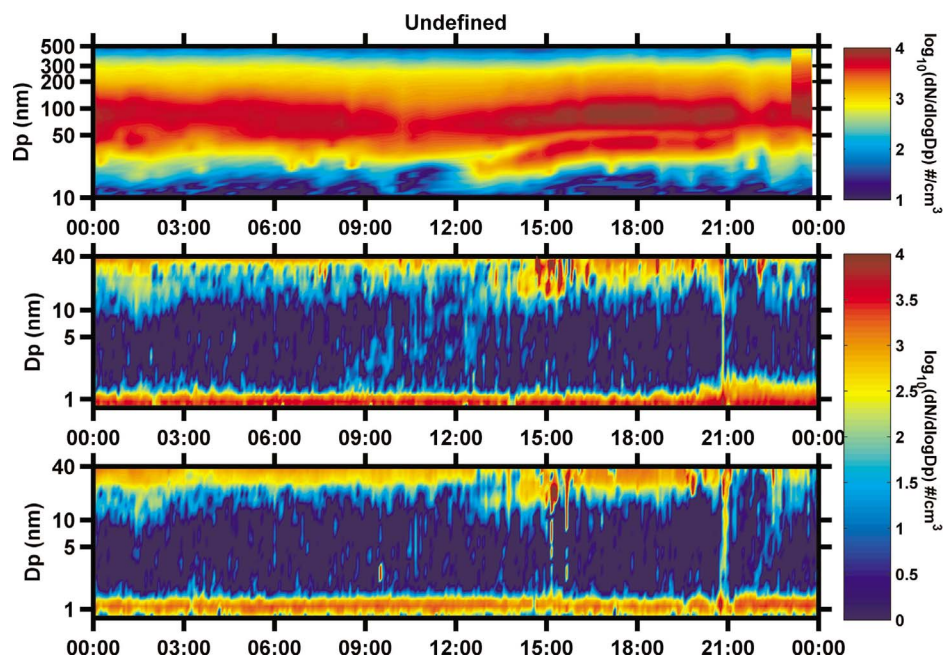
Figure 2b. SMPS and AIS measurements during an undefined day (13 May 2008) at Finokalia. (top) SMPS distribution ranging from 10 nm to 500 nm. (bottom) Positive and (middle) negative ion distributions ranging from 0.8 nm to 40 nm measured by an AIS. Time of day corresponds to local standard time (UTC+2).

end of particle formation is a lower-bound estimate. This procedure minimizes bias of new particle formation (NPF) duration due to various discrepancies such as measurement uncertainty or dispersion/dilution changes in the air mass.

[20] *Aerosol Acidity:* PM$_1$ water soluble ions at Finokalia correspond approximately to half of the mass for this size range, on an annual basis, followed by organics that account for 33% [*Koulouri et al.*, 2008]. Water soluble ions are
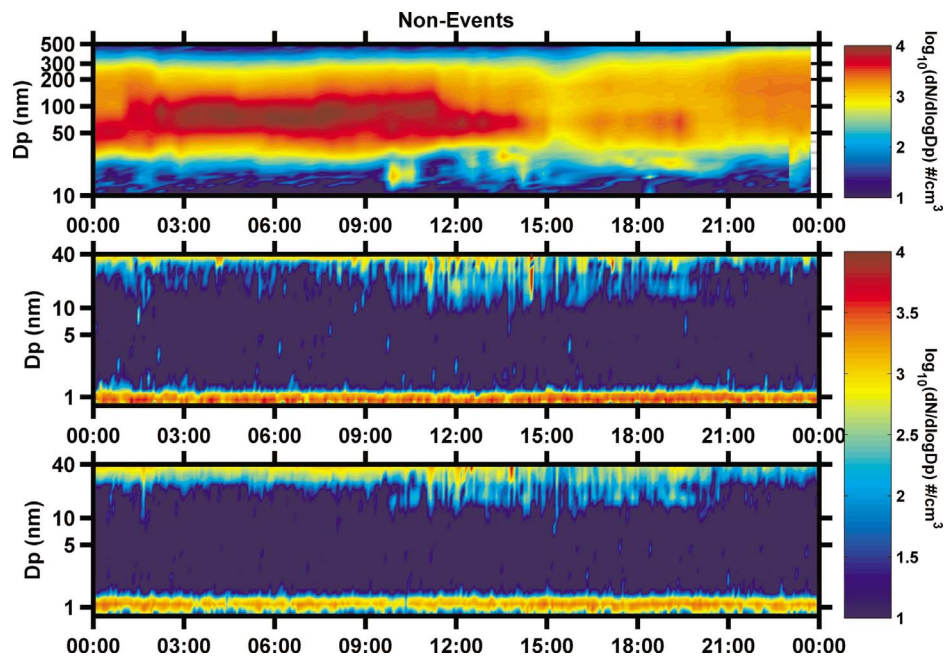
Figure 2c. SMPS and AIS measurements during a non-event day (5 May 2008) at Finokalia. (top) SMPS distribution ranging from 10 nm to 500 nm. (bottom) Positive and (middle) negative ion distributions ranging from 0.8 nm to 40 nm measured by an AIS. Time of day corresponds to local standard time (UTC+2).
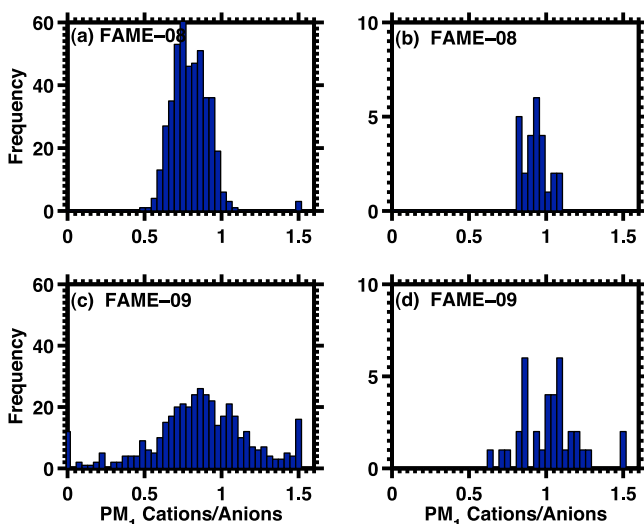
Figure 3. (a,c) PM$_1$ cations to anions ratio (in equivalents) distribution for FAME-08 and −09 from 08:00–16:00 and (b,d) the cations to anions distribution during new particle formation events and undefined events for FAME-08 and −09 based on Q-AMS measurements.

dominated by sulfate and ammonium while the concentration of other PM$_1$ ions (nitrate, chloride) is typically below 0.2 μg m^{-3}. Thus, Finokalia is a sulfate rich site, especially during the summer when PM sulfate concentrations reach their highest values and dominate the PM$_1$ composition. Unlike PM sulfate concentrations, gas phase sulfur (namely SO$_2$) concentration is typically below 1 ppb [*Bardouki et al.*, 2003]. PM$_1$ acidity at Finokalia is practically equal to the ratio of ammonium to sulfate and nitrate in molar equivalents due to lack of other ions for this size range [*Pikridas et al.*, 2010], assuming that all nitrate is inorganic. However, the ratio is not very different when we assume that all nitrate was organic (i.e., inorganic nitrate = 0) since nitrate concentrations were low. Refractory material accounts on an annual average basis for 2% of the PM$_1$ [*Koulouri et al.*, 2008]. Therefore we can exclude refractory material from our PM$_1$ acidity analysis without significant error. Using this definition of particle acidity, neutral particles have ratios equal to unity while acidic particles have ratios smaller than unity.

[21] The classification of a period as "neutral" or acidic is complicated by the measurement errors of the corresponding ion concentrations. To characterize this error we have taken advantage of the fact that the acidity ratio cannot exceed unity. Assuming that measurements are not biased and that the random error for neutral periods is normally distributed around unity, we estimated the standard deviation of the distribution based on values of the ratio exceeding unity (Figure 3). The above simplification is valid only if ammonia is the dominant basic species present to neutralize acidic particles. It is not true if other basic species, such as Ca^{2+}, compete with ammonia. This is the case during dust events when the coarse mode increases dramatically and contributes significantly even to the PM$_1$ mass [*Pikridas et al.*, 2010]. During each intensive campaign one dust

event occurred during which no nucleation events were observed, and have been excluded from our analysis.

[22] *Growth rate:* The diameter growth rates (GR) of the newly formed particles are related to the condensational flux of vapors onto the nucleation mode aerosol. Particle growth rates were determined from the AIS ion data for 1.5–3, 3–7, and 7–20 nm particles with the method introduced by *Hirsikko et al.* [2005]. First, a normal distribution function was fitted to the time series of the particle concentration in each of the AIS size channels. Then, the times (t_{max}) corresponding to the maximum concentration in the size channels (characterized by their geometric mean size D_p) were determined from the fits, and GR values were obtained by a linear least squares fit to the resulting (t_{max}, D_p) data. When the method of maximum concentrations is used, the effect of the charging rate on the estimated growth rate is small [*Yli-Juuti et al.*, 2011] provided that the charged fraction stays the same during the growth. Both polarities were analyzed separately but because of the higher negative ion concentrations our analysis will be based on them.

[23] In addition to the size-dependent GRs obtained from the AIS data, we determined daily GR values for >10 nm particles from the SMPS data. This analysis was done using the method introduced by *Dal Maso et al.* [2005], where the growth rate is determined by following the evolution of the geometric mean size of the nucleation mode.

[24] *Condensation and coagulation sink:* The capability of the existing aerosol population to remove vapors and freshly formed particles can be described by the condensational (CS) and coagulation sinks (CoagS(D_p)) respectively [*Kulmala et al.*, 2001; *Dal Maso et al.*, 2005]. CS is defined as the condensational loss rate constant of vapors, whereas CoagS(D_p) is a similar loss rate constant for particles with size D_p due to coagulation with larger particles. The values of condensation and coagulation sinks are closely coupled (both being roughly proportional to the aerosol surface area), so only the CS values were calculated to describe the background aerosol population. The CS values were calculated based on the DMPS/SMPS data and the properties of the condensable vapors are assumed to be similar to sulfuric acid, without accounting for hydration, leading to a maximum estimate.

[25] The coarse fraction (above PM$_1$) is alkaline and acts as a sink for sulfuric acid vapors, due to the reactions with sea salt and dust [*Pikridas et al.*, 2010]. Ammonium concentrations in the coarse fraction were typically low and accounted for less than 2% of the coarse mass during FAME-08 [*Pikridas et al.*, 2010] and less than 1% on an annual basis [*Koulouri et al.*, 2008]. PM$_{coarse}$ filter-based measurements were made during the FAME studies. The FAME-08 results are discussed in *Pikridas et al.* [2010]. The sea-salt concentrations in the area have also been discussed by *Mihalopoulos et al.* [1997] and *Koulouri et al.* [2008]. Briefly, the sea-salt PM$_{10}$ concentrations were a few micrograms per cubic meter and did not exceed 5 μg m^{-3}. The average PM$_1$ concentration was 10 μg m^{-3}. Therefore the coarse mode (with the exception of the dust event periods) had modest contribution (usually less than 20%) to the condensation sink.

[26] The DMPS data corresponded to dried aerosol and were corrected for the hygroscopic growth of the particles in
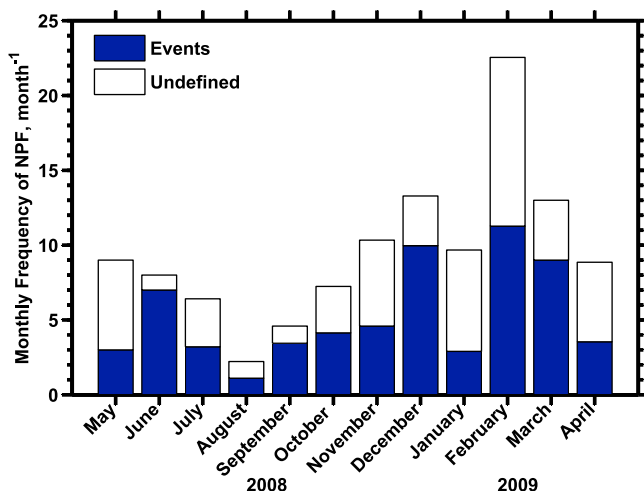
Figure 4. Monthly frequency of nucleation events and undefined events. A minimum of events and undefined is observed during August and September and a maximum in February and March.

order to calculate the CS. Water uptake was calculated using the Extended - Aerosol Inorganic Model II (E-AIM) [*Carslaw et al.*, 1995; *Clegg et al.*, 1998; *Massucci et al.*, 1999]. The inorganic $PM_{1.3}$ monthly average concentrations for sulfate, ammonium, and nitrate based on filter measurements [*Koulouri et al.*, 2008], were used as inputs for E-AIM in conjunction with RH and temperature measurements at ambient and dry conditions. The aerosol composition at Finokalia is quite stable (with the exception of dust events) and so use of the monthly average is a good first order approximation for the CS calculation. Hygroscopic growth was then estimated assuming volume additivity [*Engelhart et al.*, 2011].

3. Results and Discussion

3.1. Nucleation Event Seasonal Cycle

[27] During one year at Finokalia 58 particle formation events and 48 undefined events were observed, the monthly frequency of which is presented in Figure 4. Nucleation events are favored during the colder months (December–March) when half of the events occurred. The normalized event frequency during those months was above 8 month^{-1} with the exception of January, when seven undefined events occurred. The lowest event frequency was during August, corresponding to only one nucleation day. During the rest of the study, event frequency ranged between 3 and 6 month^{-1}. Similar low nucleation frequency during August and September has been observed in other sulfate rich regions [*Stanier et al.*, 2004]. The undefined frequency minimum occurred in September and the maximum in February, following a similar pattern as that of events.

3.2. Condensational Sink

[28] Yearly average "ambient" CS was equal to $(14 \pm 15.9) \times 10^{-3}$ s^{-1}, being 80% higher than the corresponding dry CS, which was equal to $(7.8 \pm 5.3) \times 10^{-3}$ s^{-1}. Both the "ambient" and dry annual averages are higher than the ambient CS reported for the coastal site of Mace Head

$(5.5 \times 10^{-3}$ s$^{-1})$ and Hyytiälä in the boreal forest $(4.8 \times 10^{-3}$ s$^{-1})$ [*Dal Maso et al.*, 2002]. The CS was lower on event and undefined days than non-event days (Figure 5). On average, the lowest CS values on event days occur around 08:00 (Local standard time, UTC+2), coinciding with the time nucleation events typically start, and increase linearly at a rate of 0.3×10^{-3} s^{-1} h^{-1} due to growth of both the preexisting aerosol and of the newly formed particles (Figure 5).

[29] Contrary to this overall trend, in May 2008 (FAME-08) and March 2009 (FAME-09) the CS of event days was statistically similar to the non-event ones, as shown in Table 1, suggesting that the CS was not the factor limiting nucleation during these periods.

[30] During January 2009 a small number of events are observed, as shown in Figure 4, due to the high condensational sink values of that month. Yet the seasonal variation of the CS cannot fully explain the observed NPF frequency. During August 2008 NPF frequency was at its minimum, but the highest monthly average CS was observed during October and November of the same year. CS during May 2008 and February 2009 is similar yet NPF frequency is four times higher during the latter.

3.3. Growth and Ion Formation Rates

[31] The highest daily growth rates were observed during the hottest months of the year (May 2008 to July 2008) (Table 1) reaching as high as 14 nm h^{-1} on 25 May 2008 and on 16 June 2008. The annual average growth rate of the study period was equal to 5.4 ± 3.5 nm h^{-1}. The smallest growth rates were observed during December 2008 ($\leq$2 nm h^{-1}). Daily growth rates at a boreal forest follow a similar seasonal pattern [*Dal Maso et al.*, 2005], yet the annual average is about half than that of Finokalia (3 nm h^{-1}). Size-dependent growth rates were also calculated for three size ranges; 1.5–3 nm, 3–7 nm and 7–20 nm and the average growth rate
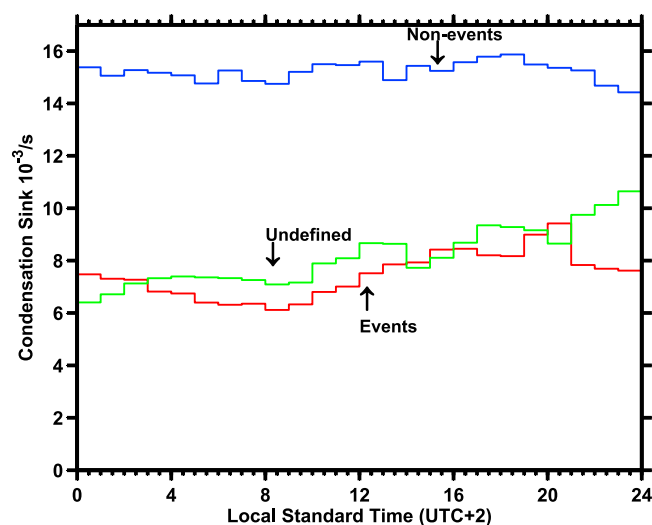

Figure 5. Average diurnal profile of the condensation sink (CS) during event (red), undefined (green) and non-event (blue) days. The CS of event and undefined days is on average about half of the CS of non-event days. The CS values are based on dry DMPS data and have been corrected for hygroscopic growth.

Table 1. Growth Rates and Condensational Sink in Finokalia During April 2008–April 2009

Month	Growth Rate (nm h^{-1})	Condensational Sink (10^{-3} s^{-1})		
		Events	Undefined	Non-Events[a]
Jan-09	4.2 ± 2.2	1.6 ± 0.1	7.6 ± 4.4	10.4 ± 9.0
Feb-09	3.1 ± 1.9	3.4 ± 1.4	4.7 ± 2.9	5.1 ± 1.8
Mar-09 (FAME-09)	4.2 ± 3.1	6.1 ± 3.5	6.4 ± 2.7	5.5 ± 3.3
Apr (08, 09)	N/A[b]	2.9[c]	8.8 ± 4.3	17.8 ± 13.1
May (FAME-08)	8.4 ± 5.2	8.5 ± 2.6	5.4 ± 1.6	8.2 ± 2.5
Jun-08	8.6 ± 4.3	6.9 ± 1.3	4.1[c]	14.8 ± 5.6
Jul-08	7.5 ± 1.2	9.1 ± 2.8	7.7 ± 5.4	10.2 ± 7.0
Aug-08	N/A[b]	N/A[b]	N/A[b]	24.2 ± 4.2
Sep-08	5.7 ± 2.7	13.5 ± 2.2	N/A[b]	16.4 ± 8.1
Oct-08	3.6 ± 1.1	13 ± 5.0	12.7 ± 13.2	26.9 ± 23.5
Nov-08	5.9 ± 2.9	5.4 ± 1.4	7 ± 5.5	39.6 ± 31.6
Dec-08	1.9 ± 0.14	2.9 ± 0.8	4.4[c]	14.5 ± 8.2
Annual Average	5.2 ± 3.4	6.5 ± 4.1	6.6 ± 4.4	15.2 ± 15.0

[a]The CS of non-events is the average CS from 08:00–16:00 (Local standard time, UTC+2).

[b]No DMPS data are available.

[c]DMPS measurements are available only for one day.

for each size range was 3.6 ± 1.1 nm h^{-1}, 6.9 ± 3.9 nm h^{-1} and 7.5 ± 5.8 nm h^{-1}, respectively. The size-dependent growth rates of the two larger size ranges typically exhibited higher values than the corresponding smaller size growth rates. The Kelvin effect is clearly one of the potential explanations for this behavior. Differences in the chemical composition of the particles can lead also to differences in the interactions between the condensing vapors and the particles and therefore affect the resulting condensation rates. Finally, it is also possible that the apparent size dependence is in fact a dependence on time. In this case the increase in the growth rates could result from a temporal increase in the concentrations of the condensable vapors. Our lack of understanding of the identity of the condensing vapors (other than sulfuric acid and ammonia) limits our ability to test the above explanations.

[32] The calculated size-dependent growth rates during one FAME-08 event and one FAME-09 event were a factor of six or more higher than the rate that can be explained by condensation of sulfuric acid. Even if this analysis is based on only two events it suggests that species other than sulfuric acid may be dominating the growth of these fresh nano-particles in Finokalia. *Riipinen et al.* [2011] reached similar conclusions for forested areas in Finland and Canada.

[33] The average ion formation rates at 2 nm in Finokalia were around 0.08 ions cm^{-3} s^{-1} for both the positive and the negative ions with a range of 0.02 to 0.1 ions cm^{-3} s^{-1}. A more detailed discussion of the growth rates and the ion formation rates for 12 European sites during the EUCAARI project can be found in *Manninen et al.* [2010].

3.4. Retroplume Analysis of New Particle Formation

[34] Nucleation is a photo-induced phenomenon, thus only the retroplumes corresponding to arrival times between 08:00 and 17:00 (Local standard time, UTC+2) were investigated. Since we used retroplumes with 3-h resolution, three retroplumes were investigated each day. The summary of the retroplume analysis is presented in Table 2. West and northwest winds favor NPF. The retroplumes which passed over Greece had the highest normalized frequency of an

event (123 year^{-1}), followed by those associated with west Crete (101 year^{-1}). The majority of source region "Greece" events were associated with the Peloponnese (southeast Greece). The normalized frequency of undefined events was independent of the origin of the air mass (Table 2).

[35] *Pikridas et al.* [2010] reported that PM$_1$ aerosol mass concentration and composition during FAME-08 were statistically similar for air masses that passed over Crete and for air masses that did not. Yet, a large difference in the normalized frequency of nucleation events exists: the frequency is much higher for air masses which passed over Crete than for those which did not. This is consistent with the hypothesis of a missing reactant which has sources over land. When the air mass does not pass over Crete, it is conceivable that this reactant is exhausted by the time that the air masses reach Finokalia and nucleation does not take place.

[36] The effect of sea breeze affecting nucleation was also examined. Because of the surrounding terrain the winds at Finokalia are consistently NW to N. Therefore no correlation among the local wind direction and events or undefined periods was noted.

3.5. Cations to Anions Ratio During Nucleation Events

[37] We would like to test the hypothesis that new particles form only when enough ammonia is present to neutralize fine particulate acids and an excess is available. Accurate measurements of gas-phase ammonia at sub-100 ppt levels are extremely difficult. We will rely instead on the accumulation mode particle acidity as an indirect measure of the availability or lack of ammonia in the gas phase. The submicrometer inorganic particles equilibrate with the gas phase in a matter of minutes [*Seinfeld and Pandis*, 1998; *Takahama et al.*, 2004]. Therefore if they are acidic, all the gas-phase ammonia has been transferred to the particulate phase (its equilibrium concentration is practically zero) and there is no gas-phase ammonia available for participation in the ternary nucleation process [*Jung et al.*, 2006]. If however, the accumulation mode particles are neutral then according to aerosol thermodynamics there can be gas-phase ammonia present. E-AIM calculations using Q-AMS measurements from different periods of the study as input showed that during the "acidic periods" the ammonia mixing ratio was below or near the 1 ppt level, while when particles were neutral the ammonia mixing ratio increased sharply near or above the ppb level. Therefore the acidity of the accumulation mode can be used as a sensitive indicator of the existence or lack there off of ammonia in the gas phase. In this case ternary nucleation should not

Table 2. Summary of Retroplume Analysis

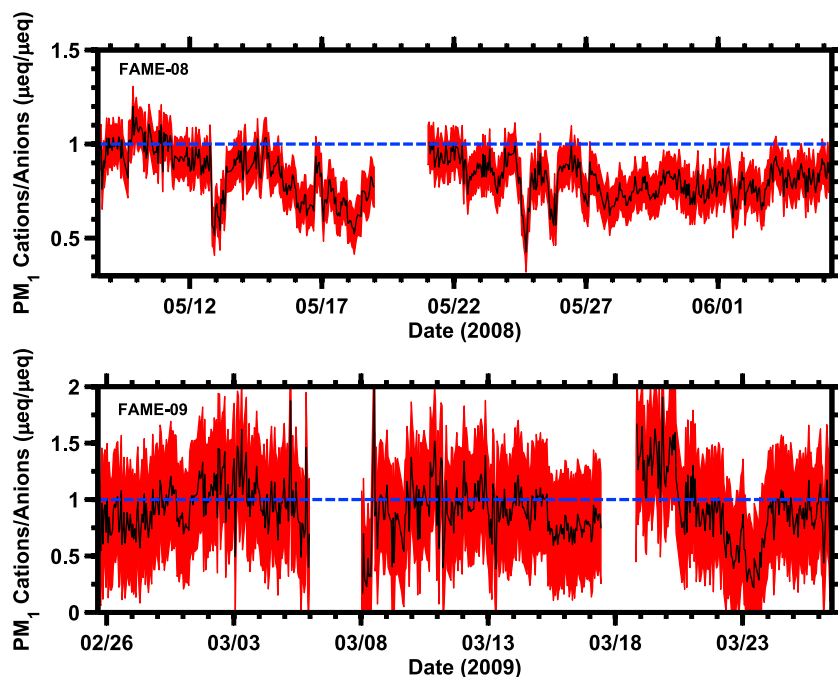|	Air Mass Origin				
	West Crete	Greece	Turkey	East Crete	Marine
Retroplumes investigated	216	161	298	185	186
Events	21	19	6	5	7
Normalized Event Frequency (year^{-1})	102	123	21	28	39
Undefined	11	6	13	10	8
Normalized Undefined Frequency (year^{-1})	53	39	39	51	45

Figure 6. Hourly averaged PM_1 cations to anions ratio during FAME -08 and -09. Red area corresponds to the estimated uncertainty (two standard deviations). Dashed line represents neutrality. Dust events have been excluded from the analysis and are not shown in these two graphs.

occur if the PM_1 is acidic. This can be tested using the AMS PM_1 composition measurements.

[38] The above argument applies to the accumulation mode particles. The coarse particles equilibrate with the gas phase much slower (timescales of hours) and therefore are not usually in equilibrium with the gas phase [*Wexler and Seinfeld*, 1992; *Meng and Seinfeld*, 1996]. This is the case often over the ocean where acidic accumulation mode particles coexist with alkaline coarse mode particles [*Capaldo et al.*, 2000]. During nucleation events the fresh particles (assuming ternary nucleation) are acidic, while the accumulation mode particles are neutral according to the simulations of *Jung et al.* [2006]. However, as the fresh particles grow to larger sizes they get neutralized by the available ammonia.

[39] The hourly averaged PM_1 cations to anions ratio (C/A) in equivalents of the two intensive campaigns (FAME-08 and FAME-09), based on Q-AMS measurements, is presented in Figure 6. The campaign-average PM_1 C/A ratio was equal to 0.85 and 0.91 for FAME-08 and FAME-09 respectively. On several occasions (usually low concentration periods), during both campaigns, the ratio exceeded unity which was attributed to measurement uncertainty. The uncertainty for the C/A ratio was estimated to be 0.08 and 0.25 for FAME-08 and FAME-09 respectively (Figure 3). The uncertainty of the FAME-09 C/A was greater than that of FAME-08 by a factor of 3 due to small PM_1 concentrations measured, which were often close to the limit of detection in the case of ammonium ($<0.1 \ \mu g \ m^{-3}$) [*Drewnick et al.*, 2009].

[40] During one third of the FAME-08 study, PM_1 C/A was below 0.84 and typically associated with air masses from Greece. On three periods the C/A ratio dropped below 0.5 (May 12 21:00 – May 13 10:00, May 24 13:20 – May 24

22:10, May 25 10:55 – May 25 23:00). On all three occasions the ratio dropped due to an increase in sulfate content which was not accompanied by an increase in ammonium. Likely the sources of sulfur include the power plants of Canakkale in Turkey and of Megalopoli in Greece as well as the city of Athens.

[41] During FAME-08, the C/A ratios during all events and "undefined" days were above 0.84 and therefore, considering the measurement uncertainty, the particles were neutral (Figure 7).

[42] As an example, the C/A ratio of the June 1 2008 nucleation event is shown in Figure 8. From midnight to 7 A.M., the C/A ratio was a little below 0.84, thus particles were acidic. The C/A ratio increased above 0.84 from 08:30 till 10:00, reaching 0.95, and new particles were formed. The event's end coincided with a sharp C/A ratio decrease after 10:00.

[43] Due to the large uncertainty of the C/A ratio during FAME-09 no definite conclusion could be drawn regarding particle acidity (Figure 6). The average PM_1 C/A of all events and undefined FAME-09 periods was above 0.9 and individual measurements within the nucleation periods were always within one standard deviation from unity (Figure 7). Both these findings suggest that the FAME-09 results are not inconsistent with our conclusions about the role of acidity.

[44] Our analysis therefore supports the hypothesis that nucleation events in this sulfate rich region occur during periods when the aerosol is neutral and NH_3 exists in the gas phase. On the other hand events do not occur, when the aerosol becomes acidic and the gas phase NH_3 is zero. While this does not prove that NH_3 is involved in particle formation it is consistent with this hypothesis. Other chemical compounds that covary with NH_3, such as amines, may also be involved. Amines are also gas-phase bases and therefore
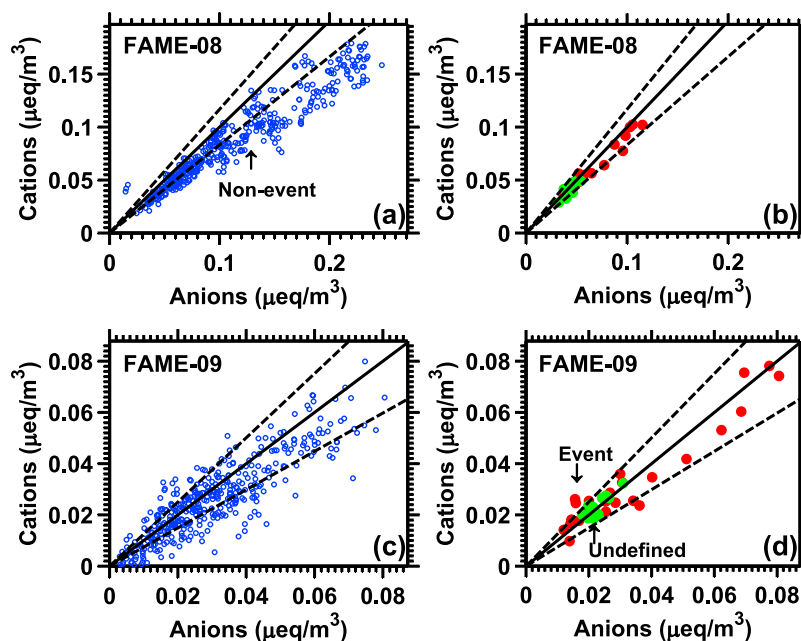
Figure 7. Cations to anions ratio for FAME-08 and -09 from 08:00 to 16:00 (UTC+2). Blue edged dots correspond to "non-events" for (a) FAME-08 and (c) FAME-09, red to "events" and green to "undefined" for (b) FAME-08 and (d) FAME-09. Dashed lines correspond to one standard deviation from unity in the case of FAME-09 and two standard deviations in the case of FAME-08. Solid line corresponds to neutral aerosol.

would have zero concentrations during periods when the fine PM is acidic.

[45] There are no noteworthy local sources of NH_3 as no major agricultural activity occurs in the area. The main source of NH_3 and ammonium is long range transport as indicated by the very good correlation of NH_4^+ with non-sea-salt sulfate ($R^2 = 0.89$ [*Koulouri et al.*, 2008]). The annual average concentration of NH_3 in the area has been reported to be 315 ± 136 ppt [*Kouvarakis et al.*, 2001].

3.6. SO_2 and Sulfuric Acid Proxy During the Two Intensive Campaigns

[46] Filter based SO_2 measurements were conducted during both intensive campaigns and are presented in Figure 9. During both campaigns, the sources of SO_2 were the same, but the photochemistry and weather differed and thus the oxidation rates were quite different.

[47] FAME-08 SO_2 measurements were presented by *Pikridas et al.* [2010]. In brief, out of the 180 analyzed samples of FAME-08, 71 were above the detection limit (20 ppt), with an average campaign concentration equal to 81 ± 70 ppt, using 20 ppt as the value for the samples which were below the detection limit. Nucleation events during that time (marked with red in Figure 9) occurred when SO_2 levels were low and typically below or near the detection limit. On several occasions during FAME-08 (such as 20 May, 24 May, 4 June and June 8) when sunlight activity was intense, SO_2 levels ranged from 200 to 300 ppt and the condensational sink was low ($4–5 \times 10^{-3}$ s^{-1}), yet no event occurred. This supports our hypothesis that nucleation at Finokalia, during FAME-08, was not limited by photochemistry, sulfuric acid production or the condensational sink.

[48] During FAME-09 average SO_2 concentrations were 211 ± 194 ppt and nucleation occurred with SO_2 concentrations ranging from 200 ppt to 450 ppt. SO_2 concentrations during FAME-09 nucleation events were more than a 10-fold higher than those of FAME-08 suggesting that SO_2 concentrations could be limiting nucleation during FAME-09.
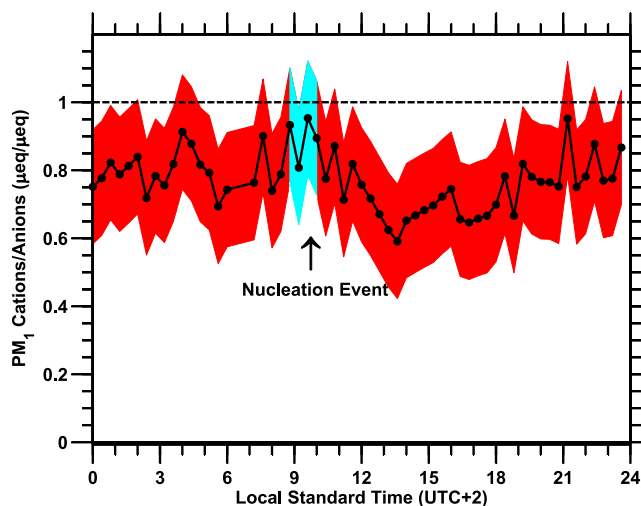

Figure 8. Cations to anions ratio during the nucleation event of 1 June 2008 at Finokalia. The beginning and end of the event is noted on the graph. Red area corresponds to the estimated uncertainty (two standard deviations). Dashed line represents neutrality. Time of day corresponds to local standard time (UTC+2).
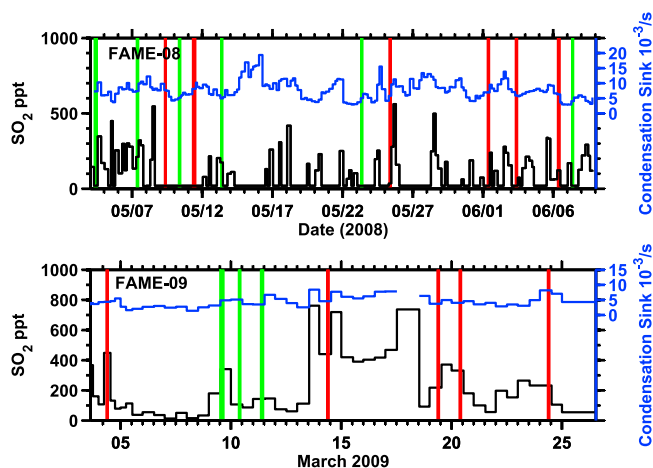
Figure 9. Filter based SO_2 measurements and condensation sink calculations during the two intensive campaigns. Red and green areas correspond to events and undefined respectively.

[49] The sulfuric acid concentration was estimated based on filter-based SO_2 measurements, photolysis frequency of NO_2 (J_{NO2}) and CS using equation (1) and is presented on Figure 10. The estimated concentrations are in fair agreement with the sulfuric acid concentrations measured during the MINOS campaign (July–August 2001) at Finokalia [*Bardouki et al.*, 2003].

[50] Nucleation events during FAME-08 (marked with red in Figure 10) occurred when the estimated H_2SO_4 concentrations were 5×10^5–2×10^6 molecules cm^{-3}, typically lower than those during undefined days (7×10^5–6×10^6 molecules cm^{-3}) and lower than the average concentration of non-event days (3×10^6 molecules cm^{-3}). This supports our hypothesis that nucleation at Finokalia, during FAME-08, was not limited by photochemistry, sulfuric acid production or the condensational sink.

[51] Contrary to FAME-08, during FAME-09 nucleation events occurred under higher ($\approx 10^7$ molecules cm^{-3}) than average ($1.2 \pm 3.0 \times 10^6$ molecules cm^{-3}) estimated sulfuric acid concentrations, indicating that sulfuric acid production was one of the factors limiting nucleation during the winter. The sulfuric acid levels during nucleation periods during the winter 2009 campaign appear to be a higher than those in the May 2008 campaign even if the condensation sinks are similar. However, the estimated levels of sulfuric acid during the winter are quite uncertain and therefore the apparent difference may be due just to this uncertainty.

3.7. Comparison With Other Coastal Nucleation Studies

[52] Nucleation in coastal areas like Mace Head has often been explained by iodine oxides [*O'Dowd et al.*, 2002a, 2002b] that are produced from the oxidation of biogenic emissions of iodine vapors. Marine algae are responsible for these emissions during low tide periods. These events are characterized by very high nucleation rates but small growth of the resulting particles to larger sizes [*O'Dowd and Hoffmann*, 2005]. Links between tidal amplitudes and coastal nucleation have been observed at various sites [*O'Dowd et al.*, 2002b; *Russell et al.*, 2007; *Whitehead*

et al., 2009]. However, other studies in coastal areas where tidal amplitude is significant have reported that the nucleation events were not related to tide height [*Modini et al.*, 2009; *Coe et al.*, 2000].

[53] The land morphology in the area around Finokalia is quite different from Mace Head with the steep slopes of the mountains extending all the way to the water. At the same time the tidal amplitude is very small. As a result, the nucleation events are very different in the two locations (e.g., the particle formation rates are orders of magnitude lower in Finokalia, the growth of the particles is quite different, etc). At Mace Head nucleation is due to a point or line source and often the growth of the nucleated particles cannot be followed [*Vana et al.*, 2008], while at Finokalia most events follow the typical "banana shape" growth pattern. In addition to these our trajectory analysis indicates that nucleation in Finokalia is favored when the air mass spends most of its time over land. If nucleation was driven by algae emissions the Marine source region should have been favored. This leads to the important conclusion that even in coastal environments the formation and growth of ultrafine particles can be quite different.

[54] Several coastal studies have taken into account the air mass history in order to explain NPF [*Coe et al.*, 2000; *Lee et al.*, 2008; *Modini et al.*, 2009]. A coastal site at west Korea has reported nucleation to be favored by westerly winds that cross the shorelines of China and Korea [*Lee et al.*, 2008]. At the Norfolk coast of the United Kingdom nucleation occurred when the air masses crossed over a certain area. It was found that the air mass was enriched with SO_2 followed by oxidation that caused nucleation [*Coe et al.*, 2000]. In the case of Finokalia, air mass history showed that west and northwest winds favored nucleation. We have assumed that the air mass is enriched with a missing reactant which we did not identify. Our analysis suggests that it could be ammonia or a species that co varies with it.

[55] At Agnes Water, Australia the air mass history was shown not to affect nucleation, but nucleation was favored
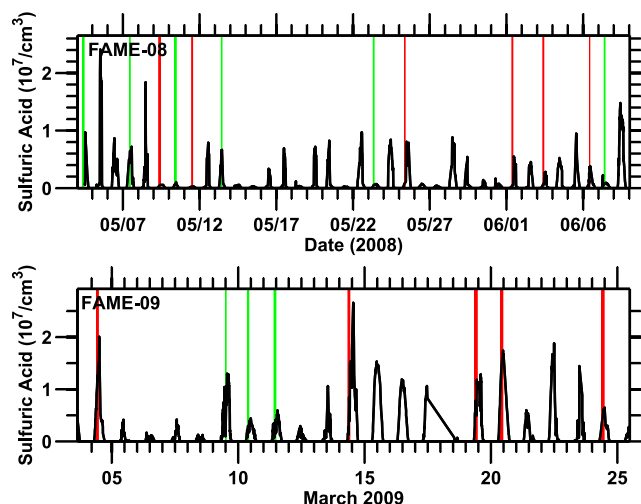

Figure 10. Sulfuric acid concentration estimated based on SO_2 measurements, photolysis frequency of NO_2 (J_{NO2}) and the condensation sink (CS). Red and green areas correspond to nucleation and undefined events, respectively.

by sea breeze [*Modini et al.*, 2009]. At Finokalia, due to the surrounding terrain the local wind direction is predominantly N-NW. As a result the wind direction patterns of events, undefined and non-events were identical.

[56] Recently it has been reported that isoprene may act as a nucleation inhibitor in clean forest environments, if the ratio of emitted isoprene to monoterpene carbon is greater or equal to 10 [*Kanawade et al.*, 2011]. However, there are few trees in the area around Finokalia (it is by no means a forest) and the surrounding flora consists of a few low-level bushes and plants that survive in this dry climate.

4. Conclusions

[57] A year of ambient particulate monitoring was conducted at a remote area in the eastern Mediterranean in order to characterize new particle formation. Particle formation periods were categorized into event, non-event, and undefined days based on their characteristics. Undefined and event days are most frequent during February and March (winter) and least frequent during August and September (summer). Nucleation events are mainly associated with air masses arriving from the west and passing over Crete, favored typically by lower than average CS. During the summer intensive campaign (FAME-08), all event and undefined particle formations occurred when particles were neutral under low SO_2 concentrations (<40 ppt) compared to the average (93 ppt).

[58] During the winter intensive campaign (FAME-09) due to the large uncertainty of the C/A ratio, almost the whole study is consistent with neutral particles. Nucleation events occurred under higher SO_2 concentrations (360 ppt) compared to the average (220 ppt) indicating that the SO_2 concentrations were limiting to some extent particle formation during that period.

[59] Our explanation of the unexpected seasonal variation of nucleation frequency (more events during the winter than during the summer) is that the availability of ammonia (or something that may covary with it like the amines) is limiting the frequency of the events. The main difference between summer and winter is that during the summer the SO_2 is oxidized fast enough so that particles are acidic most of the time. The available gas-phase ammonia is transferred to the particulate phase trying to neutralize the acid. There is more sulfate than ammonia available, so the system runs out of gas-phase ammonia. During summertime periods favorable for nucleation (high sulfuric acid, low particle surface area) the lack of ammonia (or amines) results in no nucleation events. In the winter when the photochemistry is significantly slower, there is significantly less sulfate around, so there is enough ammonia to neutralize it and some is left in the gas phase to participate in nucleation. When the right conditions appear, nucleation events take place. Air masses that pass over land just before arriving at the site can pick up ammonia and therefore nucleation is favored during these conditions.

References

Ball, S. M., D. R. Hanson, F. L. Eisele, and P. H. McMurry (1999), Laboratory studies of particle nucleation: Initial results for H_2SO_4, H_2O, and NH_3 vapors, *J. Geophys. Res.*, *104*, 23,709–23,718.

Bardouki, H., H. Berresheim, M. Vrekoussis, J. Sciare, G. Kouvarakis, K. Oikonomou, J. Schneider, and N. Mihalopoulos (2003), Gaseous (DMS, MSA, SO_2, H_2SO_4 and DMSO) and particulate (sulfate and methanesulfonate) sulfur species over the northeastern coast of Crete, *Atmos. Chem. Phys.*, *3*, 1871–1886, doi:10.5194/acp-3-1871-2003.

Benson, D. R., M. E. Erupe, and S.-H. Lee (2009), Laboratory-measured H_2SO_4-H_2O-NH_3 ternary homogeneous nucleation rates: Initial observations, *Geophys. Res. Lett.*, *36*, L15818, doi:10.1029/2009GL038728.

Benson, D. R., J. H. Yu, A. Markovich, and S.-H. Lee (2011), Ternary homogeneous nucleation of H_2SO_4, NH_3, and H_2O under conditions relevant to the lower troposphere, *Atmos. Chem. Phys.*, *11*, 4755–4766, doi:10.5194/acp-11-4755-2011.

Berndt, T., et al. (2010), Laboratory study on new particle formation from the reaction OH + SO_2: Influence of experimental conditions, H_2O vapour, NH_3 and the amine tert-butylamine on the overall process, *Atmos. Chem. Phys.*, *10*, 7101–7116, doi:10.5194/acp-10-7101-2010.

Berresheim, H., C. Plass-Dülmer, T. Elste, N. Mihalopoulos, and F. Rohrer (2003), OH in the coastal boundary layer of Crete during MINOS: Measurements and relationship with ozone photolysis, *Atmos. Chem. Phys.*, *3*, 639–649, doi:10.5194/acp-3-639-2003.

Birmili, W., F. Stratmann, and A. Wiedensohler (1999), Design of a DMA-based size spectrometer for a large particle size range and stable operation, *J. Aerosol Sci.*, *30*, 549–553, doi:10.1016/S0021-8502(98)00047-0.

Boy, M., and M. Kulmala (2002), Nucleation events in the continental boundary layer: Influence of physical and meteorological parameters, *Atmos. Chem. Phys.*, *2*, 1–16, doi:10.5194/acp-2-1-2002.

Canagaratna, M. R., et al. (2007), Chemical and microphysical characterization of ambient aerosols with the Aerodyne aerosol mass spectrometer, *Mass Spectrom. Rev.*, *26*, 185–222, doi:10.1002/mas.20115.

Capaldo, K. P., C. Pilinis, and S. N. Pandis (2000), A computationally efficient hybrid approach for dynamic gas/aerosol transfer in air quality models, *Atmos. Environ.*, *34*, 3617–3627, doi:10.1016/S1352-2310(00)00092-3.

Carslaw, K. S., S. L. Clegg, and P. Brimblecombe (1995), A thermodynamic model of the system HCl-HNO_3-H_2SO_4-H_2O, including solubilities of HBr, from <200 K to 328 K, *J. Phys. Chem.*, *99*, 11,557–11,574, doi:10.1021/j100029a039.

Charlson, R. J., and R. L. Heitzenberg (1995), *Aerosol Forcing of Climate*, John Wiley, New York.

Clegg, S., L. P. Brimblecombe, and A. S. Wexler (1998), A thermodynamic model of the system, H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O at tropospheric temperatures, *J. Phys. Chem. A*, *102*, 2137–2154, doi:10.1021/jp973042r.

Coe, H., P. I. Williams, G. McFiggans, M. W. Gallagher, K. M. Beswick, K. N. Bower, and T. W. Choularton (2000), Behavior of ultrafine particles in continental and marine air masses at a rural site in the United Kingdom, *J. Geophys. Res.*, *105*, 26,891–26,905, doi:10.1029/2000JD900234.

Coffman, D., and D. Hegg (1995), A preliminary study of the effect of ammonia on particle nucleation in the marine boundary layer, *J. Geophys. Res.*, *100*, 7147–7160, doi:10.1029/94JD03253.

Dal Maso, M., M. Kulmala, K. E. J. Lehtinen, J. M. Mäkelä, P. Aalto, and C. D. O'Dowd (2002), Condensation and coagulation sinks and formation of nucleation mode particles in coastal and boreal forest boundary layers, *J. Geophys. Res.*, *107*(D19), 8097, doi:10.1029/2001JD001053.

Dal Maso, M., M. Kulmala, I. Riipinen, R. Wagner, T. Hussein, P. Aalto, and K. E. J. Lehtinen (2005), Formation and growth of fresh atmospheric aerosols: Eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland, Boreal, *Environ. Res.*, *10*, 323–336.

DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina (1997), Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ. 97-4*, 278, Jet Propul. Lab., Pasadena, Calif.

Drewnick, F., S. S. Hings, M. R. Alfarra, A. S. H. Prevot, and S. Borrmann (2009), Aerosol quantification with the Aerodyne aerosol mass spectrometer: Detection limits and ionizer background effects, *Atmos. Meas. Tech.*, *2*, 33–46, doi:10.5194/amt-2-33-2009.

Ehn, M., et al. (2010), Composition and temporal behavior of ambient ions in the boreal forest, *Atmos. Chem. Phys.*, *10*, 8513–8530, doi:10.5194/acp-10-8513-2010.

El-Geziry, T. M. A. (2010), Environmental impact assessment and process simulation of the tidal current energy resource in the strait of Messina, PhD thesis, Dept. of Eng. and Electron., Univ. of Edinburgh, Edinburgh, U. K.

Engelhart, G. J., L. Hildebrandt, E. Kostenidou, N. Mihalopoulos, N. M. Donahue, and S. N. Pandis (2011), Water content of aged aerosol, *Atmos. Chem. Phys.*, *11*, 911–920, doi:10.5194/acp-11-911-2011.

Erupe, M. E., A. A. Viggiano, and S.-H. Lee (2011), The effect of trimethyl-lamine on atmospheric nucleation involving H_2SO_4, *Atmos. Chem. Phys.*, *11*, 4767–4775, doi:10.5194/acp-11-4767-2011.

Hildebrandt, L., et al. (2010a), Aged organic aerosol in the eastern Mediter-ranean: The Finokalia aerosol measurement experiment-2008, *Atmos. Chem. Phys.*, *10*, 4167–4186, doi:10.5194/acp-10-4167-2010.

Hildebrandt, L., E. Kostenidou, D. R. Worsnop, N. Mihalopoulos, N. M. Donahue, and S. N. Pandis (2010b), Formation of highly oxyg-ated organic aerosol in the atmosphere: Insights from the Finokalia Aero-sol Measurement Experiments, *Geophys. Res. Lett.*, *37*, L23801, doi:10.1029/2010GL045193.

Hirsikko, A., L. Laakso, U. Hõrrak, P. P. Aalto, V.-M. Kerminen, and M. Kulmala (2005), Annual and size dependent variation of growth rates and ion concentrations in boreal forest, *Boreal Environ. Res.*, *10*, 357–369.

Hirsikko, A., T. Bergman, L. Laakso, M. Dal Maso, I. Riipinen, U. Hõrrak, and M. Kulmala (2007), Identification and classification of the formation of intermediate ions measured in boreal forest, *Atmos. Chem. Phys.*, *7*, 201–210, doi:10.5194/acp-7-201-2007.

Jayne, J. T., D. C. Leard, X. F. Zhang, P. Davidovits, K. A. Smith, C. E. Kolb, and D. R. Worsnop (2000), Development of an aerosol mass spec-trometer for size and composition analysis of submicron particles, *Aero-sol Sci. Technol.*, *33*, 49–70, doi:10.1080/027868200410840.

Jimenez, J. L., R. Bahreini, D. R. Cocker III, H. Zhuang, V. Varutbangkul, R. C. Flagan, J. H. Seinfeld, C. D. O'Dowd, and T. Hoffmann (2003), New particle formation from photooxidation of diiodomethane (CH_2I_2), *J. Geophys. Res.*, *108*(D10), 4318, doi:10.1029/2002JD002452.

Jung, J., P. J. Adams, and S. N. Pandis (2006), Simulating the size distribu-tion and chemical composition of ultrafine particles during nucleation events, *Atmos. Environ.*, *40*, 2248–2259, doi:10.1016/j.atmosenv.2005.09.082.

Jung, J. G., S. N. Pandis, and P. J. Adams (2008), Evaluation of nucleation theories in a sulfur-rich environment, *Aerosol Sci. Technol.*, *42*, 495–504, doi:10.1080/02786820802187085.

Junninen, H., et al. (2010), A high-resolution mass spectrometer to measure atmospheric ion composition, *Atmos. Meas. Tech.*, *3*, 1039–1053, doi:10.5194/amt-3-1039-2010.

Kalivitis, N., W. Birmili, M. Stock, B. Wehner, A. Massling, A. Wiedensohler, E. Gerasopoulos, and N. Mihalopoulos (2008), Particle size distributions in the eastern Mediterranean troposphere, *Atmos. Chem. Phys.*, *8*, 6729–6738, doi:10.5194/acp-8-6729-2008.

Kanawade, V. P., B. T. Jobson, A. B. Guenther, M. E. Erupe, S. N. Pressley, S. N. Tripathi, and S.-H. Lee (2011) Isoprene suppression of new par-ticle formation in a mixed deciduous forest, *Atmos. Chem. Phys.*, *11*, 6013–6027, doi:10.5194/acp-11-6013-2011.

Korhonen, P., M. Kulmala, A. Laaksonen, Y. Viisanen, R. McGraw, and J. H. Seinfeld (1999), Ternary nucleation of H_2SO_4, NH_3, and H_2O in the atmosphere, *J. Geophys. Res.*, *104*, 26,349–26,353, doi:10.1029/1999JD900784.

Koulouri, E., S. Saarikoski, C. Theodosi, Z. Markaki, E. Gerasopoulos, G. Kouvarakis, T. Makela, R. Hillamo, and N. Mihalopoulos (2008), Chemical composition and sources of fine and coarse aerosol particles in the eastern Mediterranean, *Atmos. Environ.*, *42*, 6542–6550, doi:10.1016/j.atmosenv.2008.04.010.

Kouvarakis, G., K. Tsigaridis, M. Kanakidou, and N. Mihalopoulos (2000), Temporal variations of surface regional background ozone over Crete Island in the southeast Mediterranean, *J. Geophys. Res.*, *105*, 4399–4407, doi:10.1029/1999JD900984.

Kouvarakis, G., N. Mihalopoulos, T. Tselepides, and S. Stavrakakis (2001), On the importance of atmospheric nitrogen inputs on the productivity of eastern Mediterranean, *Global Biogeochem. Cycles*, *15*, 805–818, doi:10.1029/2001GB001399.

Kulmala, M., and A. Laaksonen (1990), Binary nucleation of water-sulfuric acid system: Comparison of classical theories with different H_2SO_4 satu-ration vapour pressures, *J. Chem. Phys.*, *93*, 696–701, doi:10.1063/1.459519.

Kulmala, M., L. Pirjola, and J. M. Mäkelä (2000), Stable sulphate clusters as a source of new atmospheric particles, *Nature*, *404*, 66–69, doi:10.1038/35003550.

Kulmala, M., et al. (2001), Overview of the international project on bio-genic aerosol formation in the boreal forest (BIOFOR), *Tellus, Ser. B*, *53*, 324–343, doi:10.1034/j.1600-0889.2001.530402.x.

Kulmala, M., P. Korhonen, I. Napari, A. Karlsson, H. Berresheim, and C. D. O'Dowd (2002), Aerosol formation during PARFORCE: Ternary nucleation of H_2SO_4, NH_3, and H_2O, *J. Geophys. Res.*, *107*(D19), 8111, doi:10.1029/2001JD000900.

Kulmala, M., H. Vehkamäki, T. Petaja, M. Dal Maso, A. Lauri, V.-M. Kerminen, W. Birmili, and P. H. McMurry (2004), Formation and growth rates of ultrafine atmospheric particles: A review of observa-tions, *J. Aerosol Sci.*, *35*, 143–176, doi:10.1016/j.jaerosci.2003.10.003.

Kulmala, M., K. E. J. Lehtinen, and A. Laaksonen (2006), Cluster activa-tion theory as an explanation of the linear dependence of the formation rate of 3 nm particles and sulphuric acid concentrations, *Atmos. Chem. Phys.*, *6*, 787–793, doi:10.5194/acp-6-787-2006.

Kulmala, M., et al. (2009), Introduction: European Integrated Project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI): Inte-grating aerosol research from nano to global scales, *Atmos. Chem. Phys.*, *9*, 2825–2841, doi:10.5194/acp-9-2825-2009.

Laaksonen, A., R. McGraw, and H. Vehkamäki (1999), Liquid-drop formalism and free-energy surface in binary homogeneous nucleation theory, *J. Chem. Phys.*, *111*, 2019–2027, doi:10.1063/1.479470.

Lee, Y.-G., H.-W. Lee, M.-S. Kim, C. Y. Choi, and J. Kim (2008) Charac-teristics of particle formation events in the coastal region of Korea in 2005, *Atmos. Environ.*, *42*, 3729–3739.

Lovejoy, E. R., J. Curtius, and K. D. Froyd (2004), Atmospheric ion-induced nucleation of sulfuric acid and water, *J. Geophys. Res.*, *109*, D08204, doi:10.1029/2003JD004460.

Lushnikov, A. A., and M. Kulmala (1998), Dimers in nucleating vapours, *Phys. Rev. E*, *58*, 3157–3167, doi:10.1103/PhysRevE.58.3157.

Lyubovtseva, Y. S., L. Sogacheva, M. Dal Maso, B. Bonn, P. Keronen, and M. Kulmala (2005), Seasonal variations of trace gases, meteorological parameters, and formation of aerosols in boreal forests, *Boreal Environ. Res.*, *10*, 493–510.

Manninen, H. E., et al. (2010), EUCAARI ion spectrometer measurements at 12 European sites–analysis of new-particle formation events, *Atmos. Chem. Phys.*, *10*, 7907–7927, doi:10.5194/acp-10-7907-2010.

Massucci, M., S. L. Clegg, and P. Brimblecombe (1999), Equilibrium par-tial pressures, thermodynamic properties of aqueous and solid phases, and Cl_2 production from aqueous HCl and HNO_3 and their mixtures, *J. Phys. Chem. A*, *103*, 4209–4226, doi:10.1021/jp9847179.

Meng, Z., and J. H. Seinfeld (1996), Timescales to achieve atmospheric gas-aerosol equilibrium for volatile species, *Atmos. Environ.*, *30*, 2889–2900, doi:10.1016/1352-2310(95)00493-9.

Merikanto, J., I. Napari, H. Vehkamäki, T. Anttila, and M. Kulmala (2007), New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric conditions, *J. Geophys. Res.*, *112*, D15207, doi:10.1029/2006JD007977.

Metzger, A., et al. (2010), Evidence for the role of organics in aerosol par-ticle formation under atmospheric conditions, *Proc. Natl. Acad. Sci. U. S. A.*, *107*, 6646–6651, doi:10.1073/pnas.0911330107.

Mihalopoulos, N., E. Stephanou, M. Kanakidou, S. Pilitsidis, and P. Bousquet (1997), Tropospheric aerosol ionic composition above the eastern Mediterranean area, *Tellus, Ser. B*, *49*, 314–326.

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

Modini, R. L., Z. D. Ristovski, G. R. Johnson, C. He, N. Surawski, L. Morawska, T. Suni, and M. Kulmala (2009), New particle formation and growth at a remote, sub-tropical coastal location, *Atmos. Chem. Phys.*, *9*, 7607–7621, doi:10.5194/acp-9-7607-2009.

Napari, I., M. Noppel, H. Vehkamäki, and M. Kulmala (2002), Parametriza-tion of ternary nucleation rates for H_2SO_4-NH_3-H_2O vapors, *J. Geophys. Res.*, *107*(D19), 4381, doi:10.1029/2002JD002132.

O'Dowd, C. D., and G. de Leeuw (2007), Marine aerosol production: A review of the current knowledge, *Philos. Trans. R. Soc. A*, *365*, 1753–1774, doi:10.1098/rsta.2007.2043.

O'Dowd, C. D., and T. Hoffmann (2005), Coastal new particle formation: A review of the current state-of-the-art, *Environ. Chem.*, *2*, 245–255, doi:10.1071/EN05077.

O'Dowd, C. D., L. J. Jimenez, R. Bahreini, R. C. Flagan, J. H. Seinfeld, K. Hämeri, L. Pirjola, M. Kulmala, S. G. Jennings, and T. Hoffmann (2002a), Marine aerosol formation from biogenic iodine emissions, *Nature*, *417*, 632–636, doi:10.1038/nature00775.

O'Dowd, C. D., et al. (2002b), Coastal new particle formation: Environ-mental conditions and aerosol physicochemical characteristics during nucleation bursts, *J. Geophys. Res.*, *107*(D19), 8107, doi:10.1029/2000JD000206.

Pikridas, M., et al. (2010), The Finokalia Aerosol Measurement Experi-ment–2008 (FAME-08), An overview, *Atmos. Chem. Phys.*, *10*, 6793–6806, doi:10.5194/acp-10-6793-2010.

Riipinen, I., et al. (2007), Connections between atmospheric sulphuric acid and new particle formation during QUEST III–IV campaigns in Heidel-berg and Hyytiälä, *Atmos. Chem. Phys.*, *7*, 1899–1914, doi:10.5194/acp-7-1899-2007.

Riipinen, I., et al. (2011), Organic condensation–a vital link connecting aerosol formation to climate forcing, *Atmos. Chem. Phys.*, *11*, 3865–3878, doi:10.5194/acp-11-3865-2011.

Russell, L. M., A. A. Mensah, E. V. Fischer, B. C. Sive, R. K. Varner, W. C. Keene, J. Stutz, and A. A. P. Pszenny (2007), Nanoparticle growth following photochemical a- and b-pinene oxidation at Appledore Island during International Consortium for Research on Transport and Transformation/Chemistry of Halogens at the Isles of Shoals 2004, *J. Geophys. Res.*, *112*, D10S21, doi:10.1029/2006JD007736.

Seibert, P., and A. Frank (2004), Source-receptor matrix calculation with a Lagrangian particle dispersion model in backward mode, *Atmos. Chem. Phys.*, *4*, 51–63, doi:10.5194/acp-4-51-2004.

Seinfeld, J. H., and S. N. Pandis (1998), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley, New York.

Sihto, S.-L., et al. (2006), Atmospheric sulphuric acid and aerosol formation: Implications from atmospheric measurements for nucleation and early growth mechanisms, *Atmos. Chem. Phys.*, *6*, 4079–4091, doi:10.5194/acp-6-4079-2006.

Stanier, C. O., A. Y. Khlystov, and S. N. Pandis (2004) Nucleation events during the Pittsburgh air quality study, description and relation to key meteorological, gas phase, and aerosol parameters, *Aerosol Sci. Technol.* *38*, 253–264, doi:10.1080/02786820390229570.

Stohl, A., V. Forster, A. Frank, P. Seibert, and G. Wotawa (2005), Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2, *Atmos. Chem. Phys.*, *5*, 2461–2474, doi:10.5194/acp-5-2461-2005.

Takahama, S., A. E. Wittig, D. V. Vayenas, C. I. Davidson, and S. N. Pandis (2004), Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study, *J. Geophys. Res.*, *109*, D16S06, doi:10.1029/2003JD004149.

Vana, M., M. Ehn, T. Petäjä, H. Vuollekoski, P. Aalto, G. de Leeuw, D. Ceburnis, C. D. O'Dowd, and M. Kulmala (2008), Characteristic features of air ions at Mace Head on the west coast of Ireland, *Atmos. Res.*, *90*, 278, doi:10.1016/j.atmosres.2008.04.007.

Vehkamäki, H., M. Kulmala, I. Napari, K. E. J. Lehtinen, C. Timmreck, M. Noppel, and A. Laaksonen (2002), An improved parameterization for sulfuric acid–water nucleation rates for tropospheric and stratospheric conditions, *J. Geophys. Res.*, *107*(D22), 4622, doi:10.1029/2002JD002184.

Vehkamäki, H., et al. (2004), Atmospheric particle formation events at Värriö measurement station in Finnish Lapland 1998–2002, *Atmos. Chem. Phys.*, *4*, 2015–2023, doi:10.5194/acp-4-2015-2004.

Weber, R. J., P. H. McMurry, R. L. Mauldin III, D. J. Tanner, F. L. Eisele, A. D. Clarke, and V. N. Kapustin (1999), New particle formation in the remote troposphere: A comparison of observations at various sites, *Geophys. Res. Lett.*, *26*(3), 307–310, doi:10.1029/1998GL900308.

Wen, J., Y. Zhao, and A. S. Wexler (2006), Marine particle nucleation: Observation at Bodega Bay, California, *J. Geophys. Res.*, *111*, D08207, doi:10.1029/2005JD006210.

Wexler, A. S., and J. H. Seinfeld (1992), Analysis of aerosol ammonium nitrate: Departures from equilibrium during SCAQS, *Atmos. Environ.*, *26A*, 579–591.

Whitehead, J. D., G. B. McFiggans, M. W. Gallagher, and M. J. Flynn (2009), Direct linkage between tidally driven coastal ozone deposition fluxes, particle emission fluxes, and subsequent CCN formation, *Geophys. Res. Lett.*, *36*, L04806, doi:10.1029/2008GL035969.

Yli-Juuti, T., et al. (2011), Growth rates of nucleation mode particles in Hyytiälä during 2003–2009: Variation with particle size, season, data analysis method and ambient conditions, *Atmos. Chem. Phys.*, *11*, 12,865–12,886, doi:10.5194/acp-11-12865-2011.