

1 **The role of organic condensation on ultrafine particle growth during** 2 **nucleation events**

3 D. Patoulias^{1,2}, C. Fountoukis², I. Riipinen³ and S. N. Pandis^{1,2,4}

4
5 [1] Department of Chemical Engineering, University of Patras, Patras, Greece

6 [2] Institute of Chemical Engineering Sciences, Foundation for Research and Technology Hellas
7 (FORTH/ICE-HT), Patras, Greece

8 [3] Department of Applied Environmental Science & Bert Bolin Centre for Climate Research,
9 Stockholm University, Stockholm, Sweden

10 [4] Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213,
11 USA

12 **Abstract**

13 A new aerosol dynamics model (DMANx) has been developed that simulates aerosol
14 size/composition distribution and includes the condensation of organic vapors on nanoparticles
15 through the implementation of the recently developed Volatility Basis Set framework.
16 Simulations were performed for Hyytiala (Finland) and Finokalia (Greece), two locations with
17 different organic sources where detailed measurements were available to constrain the new
18 model. We investigate the effect of condensation of organics and chemical aging reactions of
19 secondary organic aerosol (OA) precursors on ultrafine particle growth and particle number
20 concentration during a typical springtime nucleation event in both locations. This work
21 highlights the importance of the pathways of oxidation of biogenic volatile organic compounds
22 and the production of extremely low-volatility organics. At Hyytiala, organic condensation
23 dominates the growth process of new particles. The low-volatility secondary OA contributes to
24 particle growth during the early growth stage, but after a few hours most of the growth is due to
25 semi-volatile secondary OA. At Finokalia, simulations show that organics have a complementary
26 role to new particle growth contributing 45% to the total mass of new particles. Condensation of
27 organics increases the number concentration of particles that can act as CCN (N_{100}) by 13% at
28 Finokalia and 25% at Hyytiala during a typical spring day with nucleation. The sensitivity of our
29 results to the surface tension used is discussed.

30

31 **1. Introduction**

32 New particles are introduced in the atmosphere by i) direct emissions from a variety of
33 (primary) sources and, ii) nucleation (in situ formation). Nucleation and subsequent growth of
34 new particles is often observed in most areas of the globe (Kulmala et al., 2004) and represents
35 an important source of ambient aerosol number concentration. Fresh particles formed by
36 nucleation can either grow through condensation of vapors (e.g. sulfuric acid and ammonia,
37 organics) to larger sizes or can be lost by coagulation with pre-existing larger particles. The
38 newly formed particles that manage to survive coagulation can grow to larger sizes and become
39 cloud condensation nuclei (CCN) affecting the cloud droplet number concentration (Adams and
40 Seinfeld, 2002). Nucleation and subsequent growth by condensation can be an important source
41 of CCN (Lihavainen et al., 2003; Kerminen et al., 2005; Laaksonen et al., 2005; Merikanto et al.,
42 2009; Makkonen et al., 2009; Pierce and Adams, 2009b; Wang and Penner, 2009; Yu and Luo,
43 2009; Spracklen et al., 2010). Changes in CCN concentration affect cloud optical properties and
44 cloud lifetime, perturbing the energy balance of the planet (Twomey 1974; 1977; 1991; Albrecht,
45 1989). An increase of the number concentration of particles that can act as CCN results in higher
46 cloud droplet number concentrations and brighter clouds with longer lifetimes. Measurements of
47 CCN at a non-urban site in Germany suggested that CCN concentrations are mainly determined
48 by the aerosol number size distribution while the composition of aerosol plays a secondary role
49 (Dusek et al., 2006). Furthermore, nanoparticles can affect human health by deposition in the
50 human lungs or the neurological system. For small particles the damage can be greater due to the
51 larger surface area per unit mass (Peters et al., 1997; Donaldson et al, 1998; 2002). The effects of
52 aerosol composition on human health are still uncertain (Godleski et al., 2000).

53 Several mechanisms have been proposed to explain in-situ particle formation. These
54 include sulfuric acid–water binary nucleation (Nilsson and Kulmala, 1998; Vehkamäki et al.,
55 2002), ternary nucleation (Coffman and Hegg, 1995; Korhonen et al., 1999; Kulmala et al., 2002;
56 Napari et al., 2002), nucleation of organic vapors (Marti et al., 1997; Zhang et al., 2004), ion-
57 induced nucleation (Laakso et al., 2002) and halogen-oxide nucleation (Hoffmann et al., 2001).
58 The binary nucleation mechanism has been the most commonly used in atmospheric models with
59 the critical cluster assumed to be composed of H₂SO₄ and H₂O. Ternary nucleation theory
60 usually includes ammonia (NH₃) as a third component. It is possible that other compounds (e.g.
61 organics, amines) may play a similar role under certain conditions (Bonn et al., 2008; Kurten et

62 al., 2008; Metzger et al., 2010; Smith et al., 2010; Berndt et al., 2010; Zhao et al., 2011; Kirkby
63 et al., 2011; Almeida et al., 2013; Riccobono et al., 2014). A strong correlation has been found
64 between measured aerosol nucleation rate and the gas-phase sulfuric acid concentration (Weber
65 et al., 1996; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; Nieminen et al., 2009;
66 Paasonen et al., 2009; 2010) in various sites in Europe and the United States. Nucleation events
67 observed in sulfur-rich regions like the northeastern US appear to be initiated by the formation of
68 gas-phase H_2SO_4 (via SO_2 oxidation) but terminated by the exhaustion of gas-phase NH_3 or other
69 bases (Jung et al., 2008). Ambient measurements and some laboratory studies (Sipila et al.,
70 2010) have revealed a linear or squared correlation between new particle formation rate and
71 concentration of sulfuric acid.

72 Significant uncertainties arise also from the incomplete understanding of the identity of
73 the species involved in the growth of these nuclei (Kulmala et al., 2004). Field measurements
74 (Eisele and McMurry, 1997; Weber et al., 1998, 1999; Janson et al., 2001) and model
75 simulations (Kerminen et al., 2001; Kulmala et al., 2000; Pirjola and Kulmala, 2001; Anttila and
76 Kerminen, 2003) indicated that the condensation of sulfuric acid alone is often not sufficient to
77 explain the observed growth rates of fresh particles (Riipinen et al., 2011). The growth of fresh
78 nuclei could be due to the condensation of organic species (Kerminen et al., 2000; Anttila and
79 Kerminen, 2003), heterogeneous reactions (Zhang and Wexler, 2002), or ion-enhanced
80 condensation (Laakso et al., 2002).

81 Jung et al. (2010) developed a three-dimensional regional chemical transport model
82 (CTM), PMCAMx-UF, with detailed aerosol microphysics (Gaydos et al., 2007; Karydis et al.,
83 2007) that has been used for simulations over the US and Europe (Fountoukis et al., 2012). In
84 Europe the model predictions were compared against size distribution measurements from seven
85 sites (Fountoukis et al., 2012). The model was found to reproduce more than 70% of the hourly
86 number concentrations of particles larger than 10 nm (N_{10}) within a factor of 2. For particles
87 larger than 100 nm (N_{100} , a proxy for the number of particles that can act as CCN) a systematic
88 underprediction was seen. The growth rates were also underpredicted (with smaller errors in sites
89 where the sulfate to organics mass ratio is high (e.g., Melpitz)) possibly because of insufficient
90 organic vapor condensation (Fountoukis et al., 2012) as the model did not explicitly include
91 secondary organic aerosol (SOA) condensation on ultrafine particles. Yu (2011) and Riipinen et
92 al. (2011) studied the condensation of organics on ultrafine particles using global CTMs. Yu

93 (2011) estimated that the concentration of low volatility organics is a factor of 2-20 higher than
94 the H₂SO₄ concentration in many continental locations and can significantly enhance the growth
95 rate of freshly nucleated particles. He compared predicted particle size distributions with field
96 measurements in a boreal forest site (Hyytiala, Finland) showing that the condensation of low
97 volatility organics can bring the simulation results closer to the observations. Riipinen et al.
98 (2011) estimated that roughly half of the condensed organic mass needs to be distributed
99 proportionally to the aerosol surface area to explain the observed aerosol growth. These organic
100 compounds need to have both high yields and very low volatility which is inconsistent with
101 laboratory observations of the first generation yields of SOA from biogenic precursors (Presto et
102 al., 2006, Pathak et al., 2007, Pandis et al., 2013). Pierce et al. (2011) estimated that the average
103 effective saturation concentration (C^*) of condensing organics needs to be 10^{-3} – 10^{-2} $\mu\text{g m}^{-3}$ or
104 less to enhance the growth of freshly nucleated particles.

105 Secondary organic aerosol accounts for a significant mass fraction (20-90%) of sub-
106 micrometer particulate matter at many locations around the globe and is one of the most
107 dominant particle components in the atmosphere (Jimenez et al., 2009). The sources and the
108 chemical composition of OA are still uncertain due to the large number (tens of thousands) of
109 different atmospheric organic compounds (Goldstein and Galbally, 2007). OA has been the
110 subject of numerous studies during the last decade (Hallquist et al., 2009) but remains the least
111 understood component of atmospheric aerosols. The organic aerosol composition continuously
112 evolves with time due to various chemical reactions (Kanakidou et al., 2005). Gas-phase
113 oxidation of volatile organic compounds (VOCs) produces semi-volatile products that can then
114 condense to the particulate phase. Products with high vapour pressures can be oxidized to species
115 with lower vapour pressures that can then condense on preexisting particles. The chemical aging
116 (further oxidation) of semivolatile organic compounds is an important source of OA mass
117 (Donahue et al., 2006). Until recently most CTMs described secondary OA formation using two
118 surrogate species per VOC (Odum et al., 1996). This approach is computationally expensive due
119 to the large number of products while the use of only two products per VOC limits the
120 concentration range and the accuracy of this approach (Murphy et al., 2009). SOA vapors may
121 undergo further gas-phase oxidation and simulation of this aging process would require
122 introduction of even more species (Ng et al., 2006). The Volatility Basis Set (VBS) framework
123 (Donahue et al., 2006) was proposed to address these problems, describing the complete

124 volatility range of OA compounds using logarithmically spaced bins characterized by an
125 effective saturation concentration, C^* (in $\mu\text{g m}^{-3}$). This framework has been shown to work well
126 for simulations of aerosol mass distributions in 3-D CTMs (Murphy et al., 2009; Tsimpidi et al.,
127 2010; Fountoukis et al., 2011).

128 The overall objective of this work is to examine the contribution of organic vapor
129 condensation to the growth of fresh particles formed by nucleation and whether this
130 condensation can explain the observed growth rate of new particles. We extend the Dynamic
131 Model for Aerosol Nucleation (DMAN) of Jung et al. (2006) which originally assumed that
132 particles can grow only by condensation (of sulfuric acid and ammonia) and coagulation. In this
133 work, we develop an updated version of DMAN (DMANx) which includes the condensation of
134 organic vapors on particles and the most recent version of the VBS framework. We estimate for
135 the first time the effect of the chemical aging gas-phase reactions of SOA components on
136 ultrafine particle growth. We examine the effects of condensation of organics, the chemical
137 aging gas-phase reactions, and the Kelvin effect on the predicted particle number concentrations.
138 We focus on the composition of fresh particles during nucleation events as well as during their
139 subsequent growth, in two remote continental locations, Hyytiälä, Finland and Finokalia, Greece
140 where there are sufficient measurements available to constrain the new model. This is the first
141 step towards improving the predictions of the 3-D CTM, PMCAMx-UF.

142

143 **2. Model description**

144 DMAN simulates nucleation, coagulation and condensation/evaporation for a multi-
145 component atmospheric aerosol (Jung et al., 2006). It uses the Two-Moment Aerosol Sectional
146 (TOMAS) algorithm of Adams and Seinfeld (2002) which is based on the sectional approach for
147 the description of the aerosol size composition distribution. TOMAS is an adaptation of cloud
148 microphysics algorithms (Tzivion et al., 1987; 1989) to aerosol processes, is computationally
149 efficient, and tracks both mass and number concentrations simultaneously. The aerosol size
150 distribution is described with 41 size sections with the lowest size bin corresponding to a $3.75 \times$
151 10^{-25} kg dry aerosol mass per particle. That corresponds to 0.8 nm dry diameter assuming a
152 density of 1.4 g cm^{-3} . Each successive section has double the mass of the previous one. The
153 largest bin corresponds to a diameter of 10 μm .

154

155 **2.1 Nucleation**

156 DMAN has the option of using a number of nucleation parameterizations. In this work,
157 the rate of nucleation is calculated using a scaled ternary nucleation parameterization based on
158 the original expressions of Napari et al. (2002) if the NH_3 concentration exceeds 0.01 ppt, and
159 the binary parameterization of Vehkamaki et al. (2002) if it is less than this threshold value. The
160 original $\text{NH}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ parameterization has been successful in predicting the presence or lack
161 of nucleation events (Gaydos et al., 2005) in sulfur rich environments. However, it overpredicts
162 ultrafine number concentrations during nucleation events (Gaydos et al., 2005; Yu, 2006a, b;
163 Jung et al., 2006; 2008; Merikanto et al., 2007; Zhang et al., 2010) and thus a scaling factor of
164 10^{-5} is applied to the nucleation rate following Jung et al. (2010). The critical nucleus is
165 predicted to consist of roughly two molecules of sulfuric acid and two molecules of ammonia
166 (Napari et al., 2002), so it is assumed here that the newly formed particles consist of ammonium
167 bisulfate and their diameter is 1 nm.

168

169 **2.2 Gas-phase chemistry**

170 In this work, the simulation of gas phase chemistry in DMAN is updated using the
171 SAPRC99 chemical mechanism (Carter, 2000; Environ, 2003) which includes 211 reactions of
172 56 gases and 18 free radicals. It includes five lumped alkanes, two lumped olefins, two lumped
173 aromatics, isoprene, a lumped monoterpene, and a lumped sesquiterpene species. Only the two
174 highest molecular weight alkane species are considered as SOA precursors because the other
175 three contain smaller hydrocarbons (Pandis et al., 1991). OLE1 contains all the terminal alkenes,
176 while OLE2 consists of all the internal and cyclic alkenes. The major compounds for each VOC
177 class used in SAPRC99 are listed in Table S1 (Tsimpidi et al., 2010). The nine lumped VOCs
178 are considered as volatile SOA precursors with three of them being biogenic and the rest
179 anthropogenic.

180

181 **2.3 Coagulation**

182 Coagulation of particles in the atmosphere is an important sink of aerosol number but is
183 also a mechanism by which freshly nucleated particles grow to larger sizes. The TOMAS
184 algorithm is used for the simulation of coagulation. Following Adams and Seinfeld (2002),

185 TOMAS assumes that the aerosol particles coagulate via Brownian diffusion and the effects of
186 gravitational settling and turbulence are negligible. The calculation of the coagulation
187 coefficients is based on the wet diameters of the particles. These wet diameters are calculated
188 following the approach of Gaydos et al. (2005). For small particles (<100 nm), we use the
189 expression of Dahneke et al. (1983) in order to correct for non-continuum effects. The
190 coagulation algorithm uses an adaptive time step. The time step is limited so that the aerosol
191 number or mass concentration in any size category does not increase by more than an order of
192 magnitude or decrease by more than 25%.

193

194 **2.4 Condensation**

195 Condensation of gas-phase species to existing aerosol particles is an important source of
196 aerosol mass and a means by which small particles grow to CCN sizes. The TOMAS algorithm
197 is used for the simulation of condensation/evaporation of sulfuric acid, ammonia and organic
198 vapors, using the wet diameters of the particles (Gaydos et al., 2005). The driving force for
199 condensation of a vapor to an aerosol particle is the difference between its ambient vapor partial
200 pressure and the equilibrium vapor pressure over the particles, or:

$$201 \quad \Delta p_i = p_i - p_i^* x_i(D_p) \exp\left(\frac{4\sigma M_i}{RT\rho D_p}\right) \quad (1)$$

202 where Δp_i is the condensational driving force of the organic vapor i (the difference between the
203 partial pressure of condensing vapor and its equilibrium vapor pressure), p_i is the ambient partial
204 pressure, x_i is the mass fraction of i , p_i^* is the effective saturation pressure over a flat surface, σ is
205 the surface tension, M_i is the molecular weight of i , R is the ideal gas constant, T is the
206 temperature, ρ is the liquid-phase density, and D_p is the diameter of the particle. The exponential
207 term is known as the Kelvin effect due to the curvature of the particles. The exponential term is
208 large for small particles and “prevents” the condensation of organic vapors on these. As a result
209 the Kelvin effect is important for the growth of newly formed particles. We use TOMAS with an
210 adaptive time step to efficiently solve the equations for condensation. The time step is chosen so
211 that individual particles in any size bin do not grow by more than 10%, the partial pressure of the
212 organic vapor does not fall below 25% of its original value, and the time step is never longer
213 than 15 min.

214 DMANx uses the Pseudo-Steady-State Approximation (PSSA), in which the sulfuric acid
215 concentration is calculated by assuming that its production rate (oxidation of sulfur dioxide) is
216 equal to its consumption rate (condensation and nucleation). Pierce and Adams (2009a) showed
217 that the PSSA for sulfuric acid increases the computational speed with a small loss in accuracy.
218 The PSSA was tested for a variety of conditions ranging from highly polluted to extremely clean
219 conditions. Its predictions for the sulfuric acid vapor concentration and the number of new
220 particles formed during typical atmospheric nucleation events agreed well with the “benchmark
221 model” (Pierce and Adams, 2009a). Jung et al. (2010) evaluated the performance of PSSA for
222 sulfuric acid in DMAN against a 4th order Runge-Kutta algorithm and showed that PSSA is
223 accurate and computationally efficient.

224 Condensation of ammonia is simulated following the approach described by Jung et al.
225 (2006). Ammonia condensation on the ultrafine particles ends when sulfate is fully neutralized to
226 ammonium sulfate. The equilibrium ammonia vapor pressure is assumed to be zero when
227 aerosols are acidic, i.e. when the molar ratio of NH_4^+ to SO_4^{2-} is <2 . If the amount of condensed
228 ammonia exceeds the amount needed to neutralize particles during a time step, we limit the
229 maximum amount of ammonia that can condense to avoid numerical problems.

230

231 **2.5 Secondary organic aerosol formation**

232 Gas-phase oxidation of volatile organic compounds (VOCs) produces semi-volatile
233 products that can then condense to the particle phase. The VBS framework used in DMANx
234 (Donahue et al., 2006) describes the complete volatility range of OA compounds using
235 logarithmically spaced bins, characterized by an effective saturation concentration, C^* (in μg
236 m^{-3}). SOA components partition between the aerosol and gas phases, and can be formed from
237 anthropogenic SOA (aSOA) and biogenic SOA (bSOA) precursors. Each of these types is
238 simulated here with 12 volatility bins (10^{-5} – 10^6 $\mu\text{g m}^{-3}$). We assume an average molecular weight
239 of 200 gmol^{-1} for both aSOA and bSOA, while the effective enthalpies of vaporization are 30 kJ
240 mol^{-1} (Pathak et al., 2007; Stanier et al., 2007). The SOA yields used in the updated version of
241 DMAN are based on the NO_x -dependent stoichiometric yields of Murphy et al. (2009). The
242 partitioning of OA between the gas and particulate phases is approximated using vapor-liquid
243 equilibrium theory (Equation 1).

244 Semi-volatile and intermediate-volatility organics can be oxidized to species with lower
245 volatility (Donahue et al., 2006) leading to SOA production. The gas-phase chemical aging of
246 SOA precursors is modeled using a second order gas-phase reaction with the hydroxyl radical.
247 We assume that each chemical aging step reduces the volatility of the corresponding organic
248 vapor by one order of magnitude (i.e. shifting organic material from a saturation concentration of
249 e.g. 10^3 to $10^2 \mu\text{g m}^{-3}$), with a small net increase in mass (7.5%) to account for the added oxygen.
250 The chemical aging reactions for aSOA precursors are modeled with a rate constant k (298 K) =
251 $1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Murphy et al., 2009).

252 In the base case, the gas-phase chemical aging of bSOA precursors is assumed to have a
253 negligible effect on OA concentration (Lane et al., 2008). The oxidation of biogenic VOCs
254 produces semi-volatile organics with saturation concentrations of 1, 10, 10^2 and $10^3 \mu\text{g m}^{-3}$. An
255 alternative hypothesis is that the condensation of very low-volatility organics may explain the
256 observed growth. We assume that a small fraction of organics, which are produced from the
257 oxidation of biogenic VOCs, further reacts to form very low-volatility organics with a saturation
258 concentration of $C^* = 10^{-3} \mu\text{g m}^{-3}$ (Pierce et al., 2011). The sensitivity of the model results to this
259 assumption will be tested assuming a reaction converting the gas-phase surrogate species with
260 $C^* = 1 \mu\text{g m}^{-3}$ to extremely low volatility SOA with $C^* = 10^{-3} \mu\text{g m}^{-3}$ with a reasonable rate constant
261 equal to $1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. The importance of extremely low volatility organic material for
262 the growth of newly formed particles is explored in a subsequent section. This pathway is
263 consistent with the recent observations of extremely low-volatility organic compounds by Ehn et
264 al. (2014), during ozonolysis reactions as well as reactions with the hydroxyl radical.

265

266 **3. Model Application**

267 We simulated a “typical” spring day with nucleation at both Hyytiala and Finokalia. First,
268 we identified the days with observed particle formation and growth and then averaged the
269 corresponding measurements during these days generating in this way the meteorological and
270 chemical characteristics of an “average” nucleation day for the specific periods in the two
271 locations (April 2007 in Hyytiala and May 2008 in Finokalia). For the parameters for which
272 measurements were not available, but were needed for the model input, (e.g. OH concentration)
273 we followed the same process using the predicted values from the 3-D chemical transport model

274 PMCAMx (Fountoukis et al., 2015). Results are compared to the corresponding average values
275 observed during the specific periods.

276 The extended DMAN (DMANx) is first tested in Hyytiala (Finland), an environment
277 dominated by biogenic VOCs. Meteorological data, gas-phase concentrations, and aerosol
278 number distributions are available from ground measurements at the SMEAR II station in
279 Hyytiala and used here as inputs for DMANx. SMEAR II (Station for Measuring Forest
280 Ecosystem–Atmosphere Relations) is located in a rather homogenous Scots pine (*Pinus*
281 *sylvestris*) stand on flat terrain at the Hyytiala Forestry Field Station of the University of Helsinki
282 (61°51'N, 24°17'E, 181 m above sea level). The biggest city near SMEAR II is Tampere which
283 has approximately 200,000 inhabitants and is located 60 km from the measurement site. Hari and
284 Kulmala (2005) have described the station and its operation in detail. The main inputs of our
285 simulations (Table 1) are meteorological data (temperature and relative humidity), SO₂, NH₃,
286 OH, O₃, VOC concentrations and the initial aerosol number distribution. The SO₂, O₃
287 concentration, T and RH were measured continuously while the OH concentration was based on
288 the predictions of the 3-D CTM PMCAMx-2008 (Fountoukis et al., 2011). The concentrations of
289 the lumped VOCs, TERP, ISOP and ARO1 were estimated based on Proton Transfer Reaction
290 Mass Spectrometer (PTRMS) measurements. The rest of the lumped VOCs were taken from
291 PMCAMx-2008. The concentration of NH₃ was based on the measurements during the QUEST
292 IV campaign in Hyytiala (Riipinen et al., 2007). The initial aerosol number distributions are
293 available from DMPS (Differential Mobility Particle Sizer) measurements of ambient dry size
294 distributions (Aalto et al., 2001).

295 DMANx was also tested in Finokalia, a remote area in the Eastern Mediterranean region
296 with high sulfate levels and relatively low VOC concentrations. Finokalia (35° 24' N, 25° 60' E)
297 is a remote coastal station located in the southeast of the Mediterranean Sea on the island of
298 Crete in Greece. The nearest large urban center is Heraklion with 150,000 inhabitants located 50
299 km west of Finokalia. The Finokalia station is located at the top of a hill at an elevation of 230
300 m, facing the sea. There is no notable human activity at a range of approximately 15 km
301 (Kouvarakis et al., 2000). There are very few trees and little vegetation in the surrounding area.
302 Most of the aerosol at the site is transported from the surrounding regions, such as Greece,
303 Turkey and northern Africa (Pikridas et al., 2010). The concentrations of NH₃, SO₂ and aerosol
304 number distributions were based on the measurements during the Finokalia Aerosol

305 Measurement Experiment -2008 and -2009 (FAME-08 and FAME-09) (Pikridas et al., 2010;
306 2012). The other inputs (Table 1) were based on the predictions of PMCAMx.

307 The model simulates a full day beginning at midnight. In each simulation, we assumed
308 that for the initial distribution each size bin contains half organics and half ammonium sulfate.
309 Our results are not especially sensitive to this assumed initial composition; the initial particle size
310 distribution is a lot more critical..

311

312 **4. Results**

313 **4.1 Simulation without condensation of organic vapors**

314 In the simulation neglecting the organic contribution to ultrafine particle growth in
315 Hyytiala the new particles reach a diameter of 9 nm and the growth rate is only 1 nm h⁻¹
316 (Fig. 1a). The typical observed growth rates in Hyytiala are between 1-4.5 nm h⁻¹ and the final
317 diameters between 14-45 nm (Pierce et al. 2011; Yli-Juuti et al. 2011). A significant advantage
318 of DMANx is that it can track the composition of fresh particles formed by nucleation. The
319 growing nucleation mode consists of sulfate and ammonium without any organics (Fig. 1b).

320 In the Finokalia nucleation simulation, the model predicted that the fresh particles grew
321 to 32 nm with a rate of 3 nm h⁻¹ (Fig. S1a) which is less than the 5 nm h⁻¹ reported by Pikridas et
322 al. (2010; 2012). The particles reached a diameter of 10 nm at 10:00 local time. These new
323 particles consisted of sulfate and ammonium (Fig S1b). At the start of the nucleation event fresh
324 particles consist of 93% sulfate which drops to 72% by the end of the day.

325

326 **4.2 Organic condensation with $\sigma=0.025$ N m⁻¹ (no chemical aging of biogenic SOA 327 precursors)**

328 In the simulation with organic vapor condensation and $\sigma=0.025$ N m⁻¹ (Pierce et al.,
329 2011) without gas-phase chemical aging of biogenic SOA (bSOA) precursors, the predicted
330 growth rate in Hyytiala remains low at 1.2 nm h⁻¹ and the diameter of new particles at the end of
331 the day is 12 nm (Fig. 2a) These results are low compared to typical measurements of growth
332 rate in this area. The simulation showed that using a reasonable surface tension value practically
333 prevents the condensation of organics on fresh particles until they can grow above a diameter of
334 5 nm. Surface tension has also a major effect, as expected, on the composition of the new

335 particles. At the beginning of the nucleation event (Fig. 2b), the new particles do not contain any
336 organics and their initial growth is due to the condensation of sulfuric acid and ammonia. At
337 12:00 LST when the new particles have reached a diameter of 5 nm, the effect of surface tension
338 has decreased and organics start slowly condensing, contributing to growth. The mass fraction of
339 organics in the new particles gradually increases reaching 60% at the end of the day when these
340 particles reach 10 nm (Fig. 2b).

341 The organic composition of the fresh particles in Hyytiala is shown in Figure S2.
342 Components with lower volatility ($C^*=10^{-2}$ and 10^{-3} $\mu\text{g m}^{-3}$) contribute around 30% of the
343 organic mass in the initial stages of the growth (Fig. S2). Another 55% is due to the $C^*=0.1$ and 1
344 $\mu\text{g m}^{-3}$ components. As the day goes on the contribution of the more volatile components
345 increases and at the end of the day 65% of the new particle organic mass is semi-volatile material
346 (C^* of 1 and 10 $\mu\text{g m}^{-3}$). We estimate that the fraction of the condensing organic mass that has
347 gone to the ultrafine particles (diameter <100 nm) reached a maximum value of 3.5×10^{-5} at 12:00
348 LST.

349 In the case of $\sigma = 0.025 \text{ N m}^{-1}$ at Finokalia (without chemical aging of bSOA precursors),
350 the predicted growth rate is 3.8 nm h^{-1} and the new particles' diameter reaches 42 nm (Fig. S3a)
351 which is still lower than the 5 nm h^{-1} value of the measurements. At 9:30 the newly formed
352 particles consist of 90% sulfate, 6% ammonium and 4% organics (Fig. S3b). The organics
353 condensation starts accelerating later, when these particles become larger than 3 nm (after 10:00
354 LST). The predicted SOA mass fraction increases to 35% by the end of day. The surrogate OA
355 species with $C^*=1$ and 10 $\mu\text{g m}^{-3}$ were the major components of new particles in this case too,
356 representing around 70% of the OA during the day (Fig S4). In this simulation a maximum of
357 3% of condensing organic mass has gone to the ultrafine particles (at 12:00).

358

359 **4.3 Contribution of gas-phase chemical aging of biogenic SOA precursors**

360 The simulations described in the previous section (with condensation of organics and $\sigma=$
361 0.025 N m^{-1}) showed that the addition of condensation of semi-volatile organics did not close the
362 gap between predictions and field measurements of particle growth. Adding gas-phase chemical
363 aging of bSOA precursors in the Hyytiala simulation results in a growth rate of 2.2 nm h^{-1} and a
364 final diameter of 23 nm. These are very similar to the values of growth rate (2.1 nm h^{-1}) and final
365 diameter (21 nm) observed in Hyytiala on 10 April 2007 (Pierce et al., 2011) (Fig. 3). In the

366 beginning of the simulation the new particles consist mainly of ammonium sulfate and a small
367 amount of organics (Fig. 4a). This small fraction of organics is the extremely low-volatility
368 organics ($C^* = 10^{-3} \mu\text{g m}^{-3}$) produced from the aging reaction of bSOA precursors (Fig. 4b).
369 During the day the new particles grow and the mass of organics increase. The low volatility
370 material dominates the growth during the first few hours when the diameter is less than 5 nm,
371 while the semi-volatile ($C^* = 1, 10$ and $100 \mu\text{g m}^{-3}$) dominates the growth during the later stages.
372 At 18:00 LST the new particles consist mostly (90%) of organics (40% of low volatility and 60%
373 semi-volatile SOA) (Fig 4). The semi-volatile SOA contributes to growth when the particles pass
374 the size of ~ 10 nm where the Kelvin effect is small. The aging reaction affects new particles at
375 the beginning of growth when the particles are very small. The maximum mass of condensing
376 organics that has gone to the ultrafine particles is about 0.9 % at noon which is larger than in the
377 simulation without aging.

378 The assumed gas-phase aging reaction of bSOA precursors helps new particles to grow to
379 larger sizes in Finokalia too and predictions are now consistent with field measurements (Fig. 5).
380 The predicted growth rate is 4.7 nm h^{-1} while the measured growth rate in Finokalia is around 5
381 nm h^{-1} (Pikridas et al., 2012). The revised model can reproduce the observed growth rate and the
382 final particle size encouragingly well. At the start of the growth, the new particles consist of 85%
383 $(\text{NH}_4)_2\text{SO}_4$ while at the end of the day this drops to 55% (Fig. 6a). The organic components
384 initially comprise 12% of the nucleated particle mass, and are mostly of low volatility (75% is
385 from the $C^* = 10^{-3} \mu\text{g m}^{-3}$ volatility bin). During the day the organics mass fraction increases,
386 reaching a maximum of 45% of the nucleated particle mass and consisting of 30% low-volatility
387 and 70% semi-volatile organics (Fig. 6b). 4% of the condensing organics at noon has gone to the
388 ultrafine particles.

389

390 **4.4 Sensitivity analysis**

391 **4.4.1 Organic condensation neglecting the Kelvin effect without aging of bSOA precursors**

392 Condensation of organics neglecting the Kelvin effect (assuming $\sigma = 0 \text{ N m}^{-1}$) helps the
393 newly formed particles to reach a diameter of 28 nm in Hyytiala while the average growth rate is
394 1.8 nm h^{-1} (Fig. S5a). At 8:00 LST the nucleation mode particles have a size of ~ 2 nm and
395 consist of 55% sulfate, 11% ammonium and 34% organics. During the day the new particles
396 continue to grow and the fraction of organics increases to 85% at the end of the day (Fig. S5b).

397 The size of the new particles increases due to the condensation of organics. The surrogate OA
398 components with effective saturation concentration of $C^* = 1$ and $10 \mu\text{g m}^{-3}$ are predicted to be
399 the major components of the fresh particles contributing 80% of the SOA, initially, and 70% in
400 the end (Fig. S6).

401 For the Finokalia case, the predicted growth rate of new particles is 3.8 nm h^{-1} and the
402 diameter of the new fresh particles reaches 42 nm (Fig. S7a). The condensation of organics helps
403 the particles to grow faster and to reach larger sizes compared to the case described in 4.1. At
404 8:00 the particles consist of 35% organics, 5% ammonium and 60% sulfate (Fig. S7b). After
405 11:00 the new particles composition is relatively stable: 40% organics, 42% sulfate and 18%
406 ammonium. For this case of zero surface tension, organics condense immediately on the newly
407 formed particles, resulting in fast growth. In this case about 6.5% of condensing organics has
408 gone to the ultrafines at 12:00. The SOA composition is similar to that of the $\sigma = 0.025 \text{ N m}^{-1}$
409 case (Fig S8).

410

411 **4.4.2 Sensitivity of particle number concentration to surface tension**

412 So far the model showed that organic condensation can cause an increase in the size of
413 the ultrafine particles. However, large particles also grow by organic condensation resulting in
414 increased coagulation probability for the newly formed particles (Kuang et al., 2009; Westervelt
415 et al., 2013; 2014). This causes a significant reduction in the number concentration of small
416 particles compared to the case without condensation of organics. The increase of surface tension
417 leads to organic vapor condensation mostly on large particles and to a smaller extent on freshly
418 nucleated particles due to the increased Kelvin effect which prevents the condensation of
419 organics on new particles.

420 The predicted daily mean number concentration of particles above 3 nm (N_3) in Hyytiälä
421 is $3,100 \text{ cm}^{-3}$ for the simulation without organics, $5,400 \text{ cm}^{-3}$ for the zero surface tension case,
422 $2,500 \text{ cm}^{-3}$ when the organic surface tension is 0.025 N m^{-1} and $3,000 \text{ cm}^{-3}$ with the aging of
423 bSOA precursors (Fig. 7a). The maximum value of N_3 is predicted at 13:00 in all cases. For the
424 zero surface tension simulation $N_{3,\text{max}}$ is $13,500 \text{ cm}^{-3}$ while in the no-organics case $N_{3,\text{max}} = 6,300$
425 cm^{-3} . When the organic surface tension is 0.025 N m^{-1} $N_{3,\text{max}} = 4,600 \text{ cm}^{-3}$ and increases to $6,000$
426 cm^{-3} with the addition of aging of bSOA precursors (Fig. 7a).

427 At Finokalia the average predicted daily concentration of N_3 is 3600 cm^{-3} without the
428 condensation of organics and is predicted to be the same for the bSOA aging case. A similar N_3
429 is predicted for the $\sigma=0.025 \text{ N m}^{-1}$ case ($3,550 \text{ cm}^{-3}$) (Fig. S9a) while N_3 increases to 4300 cm^{-3}
430 for zero surface tension. The maximum N_3 is predicted to be the largest for the zero surface
431 tension case (Fig. S9a).

432 Neglecting the Kelvin effect in both locations allows rapid condensation of organics on
433 the fresh particles resulting in an increase of N_3 . The Kelvin effect prevents the condensation of
434 organics on new particles resulting in a decrease of N_3 . The bSOA aging and the $\sigma=0.025 \text{ N m}^{-1}$
435 simulations do not significantly affect N_3 compared to the simulation without organics.

436 The daily mean number concentration of particles above 100 nm (N_{100}) in Hyytiälä is 380
437 cm^{-3} for the no-organics case and 440 cm^{-3} for all the other simulations (Fig. 7b). In all the
438 Hyytiälä simulations with organics condensing N_{100} increases after 8:00 due to organics while in
439 the simulation without organics a smaller increase is predicted after 12:00 due to sulfuric acid
440 (Fig. 7b). Condensation of organics increased N_{100} by 25% at the end of the day.

441 A similar behavior is predicted at Finokalia. N_{100} starts increasing after 8:00 for all the
442 cases with organics condensation and after 9:00 for the no-organics case. The reason for the
443 shorter delay before the onset of N_{100} increase in the no-organics case compared to Hyytiälä is
444 that the condensation of sulfuric acid-ammonium has a predominant role in Finokalia at
445 increasing N_{100} while at Hyytiälä simulations organics dominate this growth process.
446 Furthermore, at Finokalia the concentration of sulfuric acid is higher and the photochemistry is
447 faster (much higher OH levels) than at Hyytiälä. The daily mean number concentration of
448 particles that can act as CCN (N_{100}) is predicted to be 1000 cm^{-3} without organics and 1100 cm^{-3}
449 for the other simulations (Fig. S9b). N_{100} reaches a maximum (1070 cm^{-3}) at 13:00 for the no-
450 organics case and at 18:00 in the other simulations (1210 cm^{-3}) (Fig. S9b). At the end of the day
451 N_{100} has increased by 13% due to condensation of organics. The increase of surface tension and
452 the addition of aging of bSOA precursors do not change N_{100} .

453

454 **5. Conclusions**

455 We developed an updated version of DMAN (DMANx) which includes the condensation
456 of organic vapors on ultrafine particles, using the Volatility Basis Set framework. Simulations

457 were performed for two locations with different organic sources, Hyytiala and Finokalia, during
458 a typical springtime day with aerosol nucleation and growth.

459 Using realistic values of surface tension we estimate that the semi-volatile organics
460 condensation is not enough to grow the new particles to sizes comparable to those observed.
461 Assuming that biogenic SOA precursors chemically age and produce extremely low volatility
462 organics (i.e. with an effective saturation concentration of $10^{-3} \mu\text{g m}^{-3}$) results in predicted
463 growth rates similar to those measured. In the biogenic VOC-dominated environment of
464 Hyytiala, the very low volatility organics condense onto particles smaller than 3 nm. After this
465 first-stage of growth for the new particles, the Kelvin effect becomes small and the semi-volatile
466 organics are the major components controlling the subsequent growth of the nucleated particles.
467 In an environment with more sulfuric acid and less biogenic VOCs (Finokalia) the condensation
468 of organics plays a complementary role in the growth of nucleated particles contributing 45% of
469 the total mass of new particles during a day representative of springtime nucleation.

470 The chemical gas-phase chemical aging of biogenic SOA precursors contributes to the
471 growth of the nucleated particles because of the extra mass added from the aging reactions.
472 Laboratory experiments and direct field measurements (Ehn et al., 2014) support the importance
473 of extremely low-volatility VOCs produced in the gas phase from the oxidation of monoterpenes
474 and other VOCs.

475 The condensation of organics with zero surface tension resulted in a predicted growth
476 rate similar to the field measurements, but the zero value of surface tension is unrealistic. The
477 condensation of organics with zero surface energy also affects the number concentration of
478 particles. Increasing surface tension inhibits the growth of new fresh particles and thus results in
479 a decrease of total particle number concentrations in both locations. Interestingly, when
480 including aging of bSOA precursors the new model predicts daily mean number concentrations
481 similar to those for the no-organics simulation. The number concentration of particles that can
482 act as CCN (N_{100}) increases (by 13% at Finokalia and 25% at Hyytiala) during a typical spring
483 day with nucleation, compared to the case in which the condensation of organics is neglected.
484 The increase of surface tension and the aging of bSOA precursors do not significantly affect N_{100}
485 compared to the zero surface energy case.

486

487 *Acknowledgements:* We thank Prof. Kulmala and the U. of Helsinki team for the Hyytiälä
488 measurements. This work was funded by the ARISTEIA project (National Research Excellence
489 Grant) and the ATMOPACS project (grant agreement 267099).

490

491 **6. References**

492 Aalto, P., Hameri, K., Becker, E., Weber, R., Salm, J., Mäkelä, J. M., Hoell, C., O'Dowd, C.,
493 Karlsson, H., Hansson, H. C., Vakeva, M., Koponen, I., Buzorius, G., and Kulmala, M.:
494 Physical characterization of aerosol particles during nucleation events, *Tellus*, 53B, 344–
495 358, 2001.

496 Adams, P.J., and Seinfeld, J. H.: Predicting global aerosol size distributions in general circulation
497 models, *J. Geophys. Res.*, 107, doi:10.1029/2001JD001010, 2002.

498 Albrecht, B.A.: Aerosols, cloud microphysics, and fractional cloudiness, *Science* 245, 1227–
499 1230, 1989.

500 Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, *Atmos. Environ.*, 34, 2063–2101, 2000.

501 Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, *Chem.*
502 *Rev.*, 103, 4605–4638, 2003.

503 Almeida, J., Schobesberger, S., Kurten, A., Ortega, I. K., Kupiainen-Maatta, O., Praplan, A. P.,
504 Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J.,
505 Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin,
506 A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H.,
507 Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurten, T., Kvashin, A. N.,
508 Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V.,
509 Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petaja, T., Riccobono, F.,
510 Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart,
511 S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipila, M., Stozhkov, Y., Stratmann, F.,
512 Tome, A., Trostl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala,
513 A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti,
514 T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki,
515 H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in
516 the atmosphere, *Nature*, 502, 359–363, 2013.

517 Anttila, T., and Kerminen, V.: Condensational growth of atmospheric nuclei by organic vapours,
518 *J. Aerosol Sci.*, 34, 41–61, 2003.

519 Berndt, T., Stratmann, F., Sipilä, M., Vanhanen, J., Petäjä, T., Mikkilä, J., Gruner, A.,
520 Spindler, G., Lee Mauldin III, R., Curtius, J., Kulmala, M., and Heintzenberg, J.: Laboratory
521 study on new particle formation from the reaction OH + SO₂: influence of experimental
522 conditions, H₂O vapour, NH₃ and the amine tert-butylamine on the overall process, *Atmos.*
523 *Chem. Phys.*, 10, 7101–7116, doi:10.5194/acp-10-7101-2010, 2010.

524 Bonn, B., Kulmala, M., Riipinen, I., Sihto, S. L., and Ruuskanen, T. M.: How biogenic terpenes
525 govern the correlation between sulfuric acid concentrations and new particle formation, *J.*
526 *Geophys. Res.*, 113, doi:10.1029/2007JD009327, 2008.

527 Carter, W. P. L.: Programs and files implementing the SAPRC-99 mechanism and its associated
528 emissions processing procedures for Models-3 and other regional models, January 31, 2000.

529 Coffman, D.J., and Hegg, D.A.: A preliminary study of the effect of ammonia on particle
530 nucleation in the MBL, *J. Geophys. Res.*, 100, 7147–7160, 1995.

531 Dahneke, B.: Simple kinetic theory of Brownian diffusion in vapors and aerosols, in *Theory of*
532 *Dispersed Multiphase Flow*, edited by R. E. Meyer, 97–138, Academic, San Diego, Calif.,
533 1983.

534 Donaldson, K., Li, X.Y., and Mac Nee, W.: Ultrafine (nanometer) particle mediated lung injury,
535 *J. Aerosol Sci.*, 29, 553–560, 1998.

536 Donaldson, K., Brown, D., Clouter, A., Duffin, R., MacNee, W., Renwick, L., Tran, L., and
537 Stone, V.: The pulmonary toxicology of ultrafine particles, *Journal of Aerosol Medicine*, 15,
538 213–220, 2002.

539 Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning,
540 dilution, and chemical aging of semivolatile organics, *Environ. Sci. Technol.*, 40, 2635–
541 2643, 2006.

542 Dusek, U., Frank, G. P., Hildebrandt, L., Curtius, J., Schneider, J., Walter, S., Chand, D.,
543 Drewnick, F., Hings, S., Jung, D., Borrmann, S., and Andreae, M. O.: Size matters more
544 than chemistry for cloud-nucleating ability of aerosol particles, *Science*, 312, 1375–1378,
545 2006.

546 Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, L., Springer, M., Rubach,
547 F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen,

548 T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L.
549 B., Jørgensen, S., Kjaergaard, G. H., Canagaratna, M., Dal Maso, M., Berndt, T., Petäjä, T.,
550 Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A
551 large source of low-volatility secondary organic aerosol. *Nature*, 506,
552 doi:10.1038/nature13032, 2014.

553 Eisele, F. L. and McMurry, P. H.: Recent progress in understanding particle nucleation and
554 growth, *Phil. Trans. R. Soc. Lond.*, 352, 191-201, 1997.

555 Environ, User's guide to the comprehensive air quality model with extensions (CAMx), version
556 4.02, report, ENVIRON Int. Corp., Novato, Calif, 2003.

557 Fountoukis, C., Racherla, P. N., Denier van der Gon, H. A. C., Polymeneas, P., Charalampidis,
558 P. E., Pilinis, C., Wiedensohler, A., Dall'Osto, M., O'Dowd, C., and Pandis, S. N.:
559 Evaluation of a three-dimensional chemical transport model (PMCAMx) in the European
560 domain during the EUCAARI May 2008 campaign, *Atmos. Chem. Phys.*, 11, 10331–10347,
561 2011.

562 Fountoukis, C., Riipinen, I., Denier van der Gon, H. A. C., Charalampidis, P. E., Pilinis, C.,
563 Wiedensohler, A., O'Dowd, C., Putaud, J. P., Moerman, M., and Pandis, S. N.: Simulating
564 ultrafine particle formation in Europe using a regional CTM: contribution of primary
565 emissions versus secondary formation to aerosol number concentrations, *Atmos. Chem.*
566 *Phys.*, 12, 8663-8677, 2012.

567 Gaydos, T.M., Stainer, C.O., and Pandis, S.N.: Modeling of in situ ultrafine atmospheric particle
568 formation in the eastern United State, *J. Geophys. Res.*, 110, doi:10.1029/2004JD004683,
569 2005.

570 Gaydos, T., Pinder, R., Koo, B., Fahey, K., Yarwood, G., and Pandis, S. N.: Development and
571 application of a three-dimensional Chemical Transport Model, PMCAMx, *Atmos. Environ.*,
572 41, 2594–2611, 2007.

573 Godleski, J. J., Verrier, R. L., Koutrakis, P., Catalano, P., Coull, B., Reinisch, U., Lovett, E. G.,
574 Lawrence, J., Murthy, G. G., Wolfson, J. M., Clarke, R. W., Nearing, B. D., and
575 Killingsworth, C.: Mechanisms of morbidity and mortality from exposure to ambient air
576 particles, *Res. Rep. Health Eff. Inst.*, 91, 5–103, 2000.

577 Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the earth's
578 atmosphere, *Environ. Sci. Technol.*, 41, 1514–1521, 2007.

579 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen,
580 J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann,
581 T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W.,
582 McFiggans, G., Mentel, Th. F., Monod, A., Prevt, A. S. H., Seinfeld, J. H., Surratt, J. D.,
583 Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic
584 aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, 2009.

585 Hari, P. and Kulmala, M.: Station for measuring ecosystem atmosphere relations (SMEAR II),
586 *Boreal Env. Res.*, 10, 315–322, 2005.

587 Hildebrandt, L., Donahue, N. M., and Pandis, S. N.: High formation of secondary organic aerosol
588 from the photo-oxidation of toluene, *Atmos. Chem. Phys.*, 9, 2973–2986, 2009.

589 Hoffmann, T., O’Dowd, C.D., and Seinfeld, J. H.: Iodine oxide homogeneous nucleation: an
590 explanation for coastal new particle production, *Geophys. Res. Let.*, 28, 1949–1952, 2001.

591 Janson, R., Rosman, K., Karlsson, A., and Hansson, H. C.: Biogenic emissions and gaseous
592 precursors to forest aerosols, *Tellus B*, 53, 423–440, 2001.

593 Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H.,
594 DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I.
595 M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A.,
596 Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J.,
597 Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E,
598 Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo,
599 Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D.,
600 Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y.,
601 Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C.,
602 Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E.,
603 Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere,
604 *Science*, 326, 1525–1529, 2009.

605 Jung, J., Adams, P. J., and Pandis, S. N.: Simulating the size distribution and chemical
606 composition of ultrafine particles during nucleation events, *Atmos. Environ.*, 40, 2248–
607 2259, 2006.

608 Jung, J., Adams, P. J., and Pandis, S. N.: Evaluation of nucleation theories in a sulfur-rich
609 environment, *Aerosol Sci. Technol.*, 42, 495–504, 2008.

610 Jung, J., Fountoukis, C., Adams, P. J., and Pandis, S. N.: Simulation of in situ ultrafine particle
611 formation in the eastern United States using PMCAMx-UF, *J. Geophys. Res.*, 115,
612 doi:10.1029/2009JD012313, 2010.

613 Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van
614 Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski,
615 Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K.,
616 Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling:
617 a review, *Atmos. Chem. Phys.*, 5, 1053–1123, 2005.

618 Karydis, V. A., Tsimpidi, A. P., and Pandis, S. N.: Evaluation of a three-dimensional chemical
619 transport model (PMCAMx) in the eastern United States for all four seasons, *J. Geophys.*
620 *Res.*, 112, doi:10.1029/2006JD007890, 2007.

621 Kerminen, V. M., Virkkula, A., Hillamo, R., Wexler, A. S., and Kulmala, M.: Secondary
622 organics and atmospheric cloud condensation nuclei production, *J. Geophys. Res.*, 105,
623 9255–9264, 2000.

624 Kerminen, V. M., Pirjola, L., and Kulmala, M.: How significantly does coagulative scavenging
625 limit atmospheric particle production?, *J. Geophys. Res.*, 106, 24119–24125, 2001.

626 Kerminen, V. M., Lihavainen, H., Komppula, M., Viisanen, Y., and Kulmala, M.: Direct
627 observational evidence linking atmospheric aerosol formation and cloud droplet activation,
628 *Geophys. Res. Lett.*, 32, doi:10.1029/2005GL023130, 2005.

629 Kirkby, J. et al.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric
630 aerosol nucleation, *Nature*, 476, 429–433, 2011.

631 Korhonen, P., Laaksonen, A., Viisanen, Y., McGraw, R., and Seinfeld, J. H.: Ternary nucleation
632 of H₂SO₄, NH₃, and H₂O in the atmosphere, *J. Geophys. Res.*, 104, 26349–26353, 1999.

633 Kouvarakis, G., Tsigaridis, K., Kanakidou, M., and Mihalopoulos, N.: Temporal variations of
634 surface regional background ozone over Crete Island in the southeast Mediterranean, *J.*
635 *Geophys. Res.*, 105, 4399–4407, 2000.

636 Kuang, C., McMurry, P. H., McCormick, A. V., and Eisele, F. L.: Dependence of nucleation
637 rates on sulfuric acid vapor concentration in diverse atmospheric locations, *J. Geophys. Res.*,
638 113, doi:10.1029/2007JD009253, 2008.

639 Kuang, C., McMurry, P. H., and McCormick, A. V.: Determination of cloud condensation nuclei
640 production from measured new particle formation events, *Geophys. Res. Lett.*, 36, L09822,
641 doi:10.1029/2009GL037584, 2009.

642 Kulmala, M., Pirjola, L., and Makela, J. M.: Stable sulphate clusters as a source of new
643 atmospheric particles, *Nature* 404, 66–69, 2000.

644 Kulmala, M., Korhonen, P., Napari, I., Karlsson, A., Berresheim, H., and O'Dowd, C. D.:
645 Aerosol formation during PARFORCE: ternary nucleation of H₂SO₄, NH₃, and H₂O, *J.*
646 *Geophys. Res.*, 107, doi:10.1029/2001JD000900, 2002.

647 Kulmala, M., Vehkamäki, H., Petaja, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W.,
648 and McMurry, P. H.: Formation and growth of ultrafine atmospheric particles: A review of
649 observations, *J. Aerosol Sci.*, 35, 143–176, 2004.

650 Kurten, T., Loukonen, V., Vehkamäki, H., and Kulmala, M.: Amines are likely to enhance
651 neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively
652 than ammonia, *Atmos. Chem. Phys.*, 8, 4095–4103, 2008.

653 Laakso, L., Makela, J. M., Pirjola, L., and Kulmala, M.: Model studies on ion – induced
654 nucleation in the atmosphere, *J. Geophys. Res.*, 107, doi:10.1029/2002JD002140, 2002.

655 Laaksonen, A., Hamed, A., Joutsensaari, J., Hiltunen, L., Cavalli, F., Junkermann, W., Asmi, A.,
656 Fuzzi, S., and Facchini, M. C.: Cloud condensation nucleus production from nucleation
657 events at a highly polluted region, *Geophys. Res. Lett.*, 32, doi:10.1029/2004GL022092,
658 2005.

659 Lane, T. E., Donahue, N. M., and Pandis, S. N.: Simulating secondary organic aerosol formation
660 using the volatility basis-set approach in a chemical transport model, *Atmos. Environ.*, 42,
661 7439–7451, 2008.

662 Lihavainen, H., Kerminen, V. M., Komppula, M., Hatakka, J., Aaltonen, V., Kulmala, M., and
663 Viisanen, Y.: Production of “potential” cloud condensation nuclei associated with
664 atmospheric new particle formation in northern Finland, *J. Geophys. Res.*, 108,
665 doi:10.1029/2003JD003887, 2003.

666 Makkonen, R., Asmi, A., Korhonen, H., Kokkola, H., Jarvenoja, S., Raisanen, P., Lehtinen, K. E.
667 J., Laaksonen, A., Kerminen, V. M., Jarvinen, H., Lohmann, U., Bennartz, R., Feichter, J.,
668 and Kulmala, M.: Sensitivity of aerosol concentrations and cloud properties to nucleation

669 and secondary organic distribution in ECHAM5-HAM global circulation model, *Atmos.*
670 *Chem. Phys.*, 9, 1747–1766, 2009.

671 Marti, J. J., Weber, R. J., McMurry, P. H., Eisele, F., Tanner, D., and Jefferson, A.: New particle
672 formation at a remote continental site, assessing the contributions of SO₂ and organic
673 precursors, *J. Geophys. Res.*, 102, 6331–6339, 1997.

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

677 Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., and Carslaw, K. S.: Impact of
678 nucleation on global CCN, *Atmos. Chem. Phys.*, 9, 8601–8616, 2009.

679 Metzger, A., Verheggen, B., Dommen, J., Duplissy, J., Prevot, A. S. H., Weingartner, E.,
680 Riipinen, I., Kulmala, M., Spracklen, D. V., Carslaw, K. S., and Baltensperger, U.: Evidence
681 for the role of organics in aerosol particle formation under atmospheric conditions, *Proc.*
682 *Natl. Acad. Sci.*, 107, 6646–6651, 2010.

683 Murphy, B. N. and Pandis, S.N.: Simulating the formation of semivolatile primary and secondary
684 organic aerosol in a regional chemical transport model, *Environ. Sci. Technol.*, 43, 4722–
685 4728, 2009.

686 Napari, I., Noppel, M., Vehkamäki, H., and Kulmala, M.: Parameterization of ternary nucleation
687 rates for H₂SO₄-NH₃-H₂O vapors, *J. Geophys. Res.*, 107, doi:10.1029/2002JD002132, 2002.

688 Ng, N. L., Kroll, J. H., Keywood, M. D., Bahreini, R., Varutbangkul, V., Flagan, R. C., Seinfeld,
689 J. H., Lee, A. and Goldstein, A. H.: Contributions of first- versus second-generation
690 products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons,
691 *Environ. Sci. Technol.*, 40, 2283–2297, 2006.

692 Nieminen, N., Manninen, H. E., Sihto, S. L., Yli-Juuti, T., Mauldin, R. L., Petaja, T., Riipinen, I.,
693 Kerminen, V.-M., and Kulmala, M.: Connection of sulfuric acid to atmospheric nucleation
694 in boreal forest, *Environ. Sci. Technol.*, 43, 4715–4721, 2009.

695 Nilsson, E.D., and Kulmala, M.: The potential for atmospheric mixing processes to enhance the
696 binary nucleation rate, *J. Geophys. Res.*, 103, 1381–1389, 1998.

697 Odum, J. R., Hoffman, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H.:
698 Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.*, 30,
699 2580–2585, 1996.

700 Paasonen, P., Sihto, S. L., Nieminen, T., Vuollekoski, H., Riipinen, I., Plass-Dulmer, C.,
701 Berresheim, H., Birmili, W., and Kulmala, M.: Connection between new particle formation
702 and sulphuric acid at Hohenpeissenberg (Germany) including the influence of organic
703 compounds, *Boreal Environ. Res.*, 14, 616–629, 2009.

704 Paasonen, P., Nieminen, T., Asmi, E., Manninen, H. E., Petaja, T., Plass-Dulmer, C., Flentje, H.,
705 Birmili, W., Wiedensohler, A., Horrak, U., Metzger, A., Hamed, A., Laaksonen, A.,
706 Facchini, M. C., Kerminen, V.-M., and Kulmala, M.: On the roles of sulphuric acid and low-
707 volatility organic vapours in the initial steps of atmospheric new particle formation, *Atmos.*
708 *Chem. Phys.*, 10, 11223–11242, 2010.

709 Pandis, S. N., Paulson, S. E., Seinfeld, J. H., and Flagan, R.C.: Aerosol formation in the
710 photooxidation of isoprene and α -pinene, *Atmos. Environ.*, 25A, 997–1008, 1991.

711 Pandis, S. N., Donahue, N. M., Murphy, B. N., Riipinen, I., Fountoukis, C., Karnezis, E., Patoulias,
712 D., and Skyllakou, K.: Atmospheric organic aerosols: insights from the combination of
713 measurements chemical transport models, *Faraday Discuss.*, doi:10.1039/c3fd00108c, 2013.

714 Pathak, R. K., Presto, A. A., Lane, T. E., Stanier, C. O., Donahue, N. M., and Pandis, S. N.:
715 Ozonolysis of R-pinene: parameterization of secondary organic aerosol mass fraction,
716 *Atmos. Chem. Phys.*, 7, 3811–3821, 2007.

717 Peters, A., Wichmann, H. E., Tuch T., Heinrich J., and Heyder J.: Respiratory effects are
718 associated with the number of ultrafine particles, *Am. J. Respir. Crit. Care Med.*, 155, 1376–
719 1383, 1997.

720 Presto, A. A., Donahue, N. M.: Investigation of α -pinene + ozone secondary organic aerosol
721 formation at low total aerosol mass, *Environ. Sci. Technol.*, 40, 3536–3543, 2006.

722 Pierce, J. R. and Adams, P. J.: A computationally efficient aerosol nucleation/condensation
723 method: Pseudo-steady state sulfuric acid, *Aerosol Sci. Technol.*, 43, 216–226, 2009a.

724 Pierce, J. R. and Adams, P. J.: Uncertainty in global CCN concentrations from uncertain aerosol
725 nucleation and primary emission rates, *Atmos. Chem. Phys.*, 9, 1339–1356, 2009b.

726 Pierce, J. R., Riipinen, I., Kulmala, M., Ehn, M., Petaja, T., Junninen, H., Worsnop, D. R., and
727 Donahue, N. M.: Quantification of the volatility of secondary organic compounds in
728 ultrafine particles during nucleation events, *Atmos. Chem. Phys.*, 11, 9019–9036, 2011.

729 Pirjola, L., and Kulmala, M.: Development of particle size and composition distributions with a
730 novel aerosol dynamics model, *Tellus B*, 53, 491–509, 2001.

731 Pikridas, M., Bougiatioti, A., Hildebrandt, L., Engelhart, G. J., Kostenidou, E., Mohr, C.,
732 Prévôt, A. S. H., Kouvarakis, G., Zampas, P., Burkhardt, J. F., Lee, B.-H., Psichoudaki, M.,
733 Mihalopoulos, N., Pilinis, C., Stohl, A., Baltensperger, U., Kulmala, M., and Pandis, S. N.:
734 The Finokalia Aerosol Measurement Experiment – 2008 (FAME-08): an overview, *Atmos.*
735 *Chem. Phys.*, 10, 6793-6806, 2010.

736 Pikridas M., Riipinen, I., Hildebrandt, L., Kostenidou, E., Manninen, H., Mihalopoulos, N.,
737 Kalivitis, N., Burkhardt, J. F., Stohl, A., Kulmala, M., and Pandis, S. N.: New particle
738 formation at a remote marine site in the Eastern Mediterranean, *J. Geophys. Res.*, 117,
739 doi:10.1029/2012JD017570, 2012.

740 Riccobono, F., Schobesberger, S., Scott, C. E., Dommen, J., Ortega, I. K., Rondo, L., Almeida,
741 J., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Downard, A., Dunne, E. M.,
742 Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hansel, A., Junninen, H., Kajos, M.,
743 Keskinen, H., Kupc, A., Kürten, A., Kvashin, A. N., Laaksonen, A., Lehtipalo, K.,
744 Makhmutov, V., Mathot, S., Nieminen, T., Onnela, A., Petäjä, T., Praplan, A. P., Santos, F.
745 D., Schallhart, S., Seinfeld, J. H., Sipilä, M., Spracklen, D. V., Stozhkov, Y., Stratmann, F.,
746 Tomé, A., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Vrtala, A., Wagner, P. E.,
747 Weingartner, E., Wex, H., Wimmer, D., Carslaw, K. S., Curtius, J., Donahue, N. M.,
748 Kirkby, J., Kulmala, M., Worsnop, D. R., and Baltensperger, U.: Oxidation products of
749 biogenic emissions contribute to nucleation of atmospheric particles, *Science*, 344, 717-
750 721, 2014.

751 Riipinen, I., Sihto, S.-L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K.,
752 Teinila, K., Kerminen, V.-M., Laaksonen, A., and Lehtinen, K. E. J.: Connections between
753 atmospheric sulphuric acid and new particle formation during QUEST III–IV campaigns in
754 Heidelberg and Hyytiälä, *Atmos. Chem. Phys.*, 7, 1899–1914, 2007.

755 Riipinen, I., Pierce, J. R., Yli-Juuti, T., Nieminen, T., Hakkinen, S., Ehn, M., Junninen, H.,
756 Lehtipalo, K., Petaja, T., Slowik, J., Chang, R., Shantz, N. C., Abbatt, J., Leaitch, W. R.,
757 Kerminen, V.-M., Worsnop, D. R., Pandis, S. N., Donahue, N. M., and Kulmala, M.:
758 Organic condensation: a vital link connecting aerosol formation to cloud condensation
759 nuclei (CCN) concentrations, *Atmos. Chem. Phys.*, 11, 3865–3878, 2011.

760 Sihto, S. L., Kulmala, M., Kerminen, V. M., Dal Maso, M., Petaja, T., Riipinen, I., Korhonen,
761 H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J.: Atmospheric

762 sulphuric acid and aerosol formation: implications from atmospheric measurements for
763 nucleation and early growth mechanisms, *Atmos. Chem. Phys.*, 6, 4079–4091, 2006.

764 Sipila, M., Berndt, T., Petaja, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin
765 III, R. L., Hyvarinen, A.-P., Lihavainen, H., and Kulmala, M.: Role of sulfuric acid in
766 atmospheric nucleation, *Science*, 327, 1243–1246, 2010.

767 Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J.
768 H., Williams, B. J., and Mc-Murry, P. H.: Observations of ammonium salts in atmospheric
769 nanoparticles and possible climatic implications, *P. Natl. Acad. Sci. USA*, 107, 6634–6639,
770 2010.

771 Spracklen, D. V., Carslaw, K. S., Merikanto, J., Mann, G. W., Reddington, C. L., Pickering, S.,
772 Ogren, J. A., Andrews, E., Baltensperger, U., Weingartner, E., Boy, M., Kulmala, M.,
773 Laakso, L., Lihavainen, H., Kivekas, N., Komppula, M., Mihalopoulos, N., Kouvarakis, G.,
774 Jennings, S. G., O’Dowd, C., Birmili, W., Wiedensohler, A., Weller, R., Gras, J., Laj, P.,
775 Sellegri, K., Bonn, B., Krejci, R., Laaksonen, A., Hamed, A., Minikin, A., Harrison, R. M.,
776 Talbot, R., and Sun, J.: Explaining global surface aerosol number concentrations in terms of
777 primary emissions and particle formation, *Atmos. Chem. Phys.*, 10, 4775–4793, 2010.

778 Stanier, C. O., Pathak, R. K., and Pandis, S. N.: Measurements of the volatility of aerosols from
779 α -pinene ozonolysis, *Environ. Sci. Technol.*, 41, 2756–2763, 2007.

780 Twomey, S.: Pollution and the planetary albedo, *Atmos. Environ.*, 8, 1251–1256, 1974.

781 Twomey, S.: The Influence of pollution on the shortwave albedo of clouds, *J. Atmos. Sci.*, 34,
782 1149–1152, 1977.

783 Twomey, S.: Aerosols, clouds, and radiation, *Atmos. Environ.*, 25A, 2435–2442, 1991.

784 Tzivion, S., Feingold, G., and Levin, Z.: An efficient numerical solution to the stochastic
785 collection equation, *J. Atmos. Sci.*, 44, 3139–3149, 1987.

786 Tzivion, S., Feingold, G., and Levin, Z.: The evolution of raindrop spectra. Part II: collisional
787 collection/breakup and evaporation in a rain shaft, *Journal of the Atmospheric Sciences*, 46,
788 3312–3327, 1989.

789 Tsimpidi, A. P., Karydis, V. A., Zavala, M., Lei, W., Molina, L., Ulbrich, I. M., Jimenez, J. L.,
790 and Pandis, S. N.: Evaluation of the volatility basis-set approach for the simulation of
791 organic aerosol formation in the Mexico City metropolitan area, *Atmos. Chem. Phys.*, 10,
792 525–546, 2010.

793 Vehkamäki, H., Kulmala, M., Napari, I., Lehtinen, K. E. J., Timmreck, C., Noppel, M., and
794 Laaksonen, A.: An improved parameterization for sulfuric acid-water nucleation rates for
795 tropospheric and stratospheric conditions, *J. Geophys. Res.*, 107, 4622–4632, 2002.

796 Wang, M. and Penner, J. E.: Aerosol indirect forcing in a global model with particle nucleation,
797 *Atmos. Chem. Phys.*, 9, 239–260, 2009.

798 Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, T. J., and Jefferson, A.:
799 Measured atmospheric new particle formation rates: Implications for nucleation
800 mechanisms, *Chem. Eng. Commun.*, 151, 53–64, 1996.

801 Weber, R.J., et al.: A study of new particle formation and growth involving biogenic and trace
802 gas species measured during ACE 1, *J. Geophys. Res.*, 103, 16385–16396, 1998.

803 Weber, R.J., et al.: New particle formation in the remote troposphere: a comparison of
804 observations at various sites, *Geophys. Res. Lett.*, 26, 307–310, 1999.

805 Westervelt, D. M., Pierce, J. R., Riipinen, I., Trivittayanurak, W., Hamed, A., Kulmala, M.,
806 Laaksonen, A., Decesari, S., and Adams, P. J.: Formation and growth of nucleated particles
807 into cloud condensation nuclei: model-measurement comparison, *Atmos. Chem. Phys.*, 13,
808 7645–7663, 2013.

809 Westervelt, D. M., Pierce, J. R., and Adams, P. J.: Analysis of feedbacks between nucleation
810 rate, survival probability and cloud condensation nuclei formation, *Atmos. Chem. Phys.*, 14,
811 5577–5597, 2014.

812 Yli-Juuti, T., Nieminen, T., Hirsikko, A., Aalto, P. P., Asmi, E., Horrak, U., Manninen, H. E.,
813 Patokoski, J., Dal Maso, M., Petaja, T., Rinne, J., Kulmala, M., and Riipinen, I.: Growth
814 rates of nucleation mode particles in Hyytiälä during 2003– 2009: variation with particle
815 size, season, data analysis method and ambient conditions, *Atmos. Chem. Phys.*, 11, 12865–
816 12886, 2011.

817 Yu, F.: Effect of ammonia on new particle formation: A kinetic $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ nucleation
818 model constrained by laboratory measurements, *J. Geophys. Res.*, 111,
819 doi:10.1029/2005JD005968, 2006a.

820 Yu, F.: From molecular clusters to nanoparticles: second-generation ion-mediated nucleation
821 model, *Atmos. Chem. Phys.*, 6, 5193–5211, 2006b.

822 Yu, F. and Luo, G.: Simulation of particle size distribution with a global aerosol model:
823 contribution of nucleation to aerosol and CCN number concentrations, *Atmos. Chem. Phys.*,
824 9, 7691–7710, 2009.

825 Yu, F.: A secondary organic aerosol formation model considering successive oxidation aging and
826 kinetic condensation of organic compounds: global scale implications, *Atmos. Chem. Phys.*,
827 11, 1083–1099, 2011.

828 Zhang, K.M., and Wexler, A.S.: A hypothesis for condensation of fresh atmospheric nuclei,
829 *Journal of Geophysical Research*, 107, doi:10.1029/2002JD002180, 2002.

830 Zhang, R.I., et al.: Atmospheric new particle formation enhanced by organic acids, *Science*, 304,
831 1487–1490, 2004.

832 Zhang, Y., McMurry, P. H., Yu, F., and Jacobson, M. Z.: A comparative study of nucleation
833 parameterizations: 1. Examination and evaluation of the formulations, *J. Geophys. Res.*,
834 115, doi:10.1029/2010JD014150, 2010.

835 Zhao, J., Smith, J. N., Eisele, F. L., Chen, M., Kuang, C., and McMurry, P. H.: Observation of
836 neutral sulfuric acid-amine containing clusters in laboratory and ambient measurements,
837 *Atmos. Chem. Phys.*, 11, 10823–10836, 2011.

838

839 **Table 1.** Main inputs of DMANx simulations.

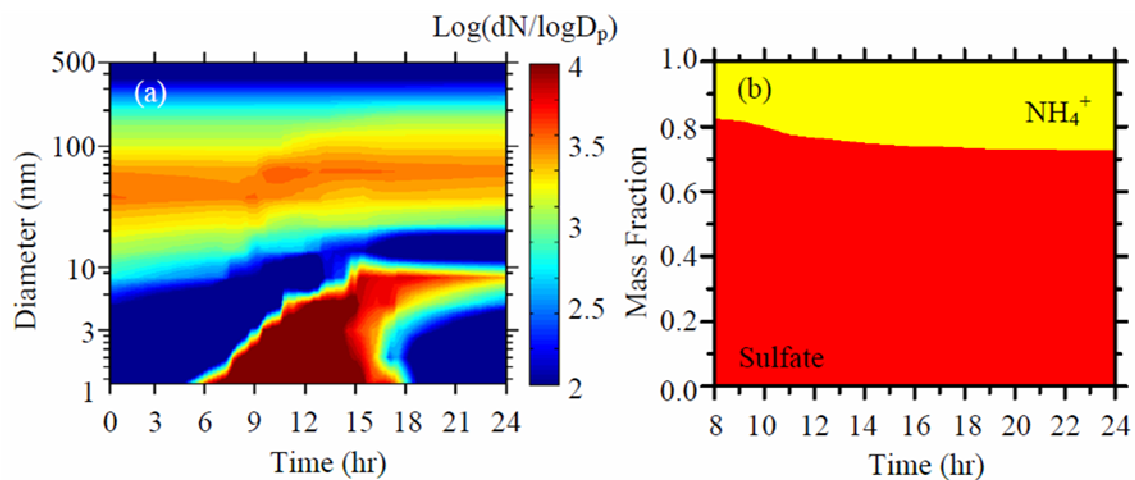
Inputs	Hyytiälä (Finland)	Finokalia (Greece)
Temperature	Measurements	Model PMCAMx
RH	Measurements	Model PMCAMx
O ₃	Measurements	Model PMCAMx
OH	Model PMCAMx	Model PMCAMx
SO ₂	Measurements	Measurements
NH ₃	Measurements (PTR-MS)	Measurements
TERP	Measurements (PTR-MS)	Model PMCAMx
ISOP	Measurements (PTR-MS)	Model PMCAMx
ARO1	Measurements (PTR-MS)	Model PMCAMx
ARO2	Model PMCAMx	Model PMCAMx
ALK4	Model PMCAMx	Model PMCAMx
ALK5	Model PMCAMx	Model PMCAMx
Initial number distributions	Measurements (DMPS)	Measurements (SMPS)

840

841

842

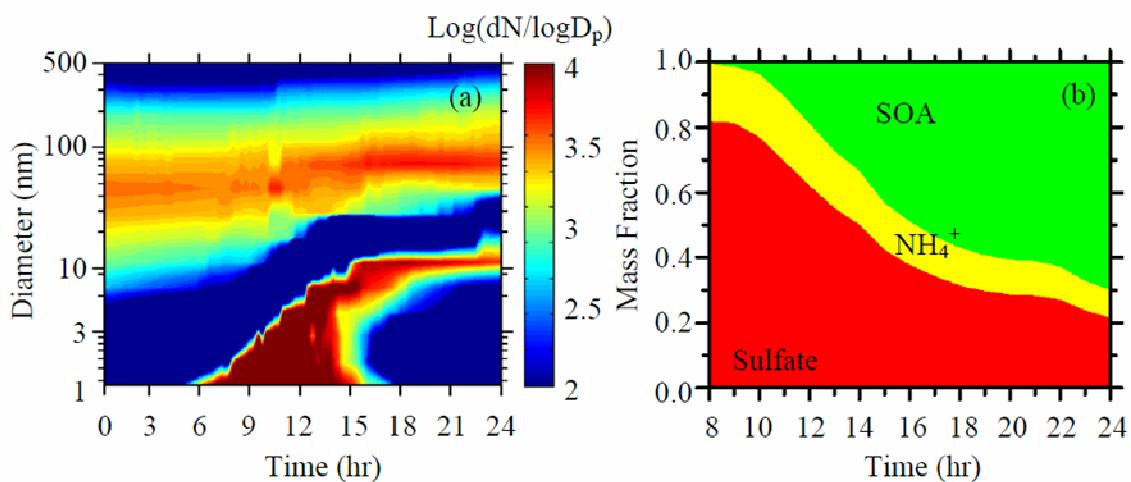
843
844
845
846
847
848
849
850
851
852
853
854



855 **FIGURE 1:** a) Predicted aerosol dry size distribution for a typical spring nucleation event at
856 Hyttiala without condensation of organics. Particle number concentration is plotted against local
857 time of day (x-axis) and particle diameter (y-axis). b) Predicted composition of new particles.
858

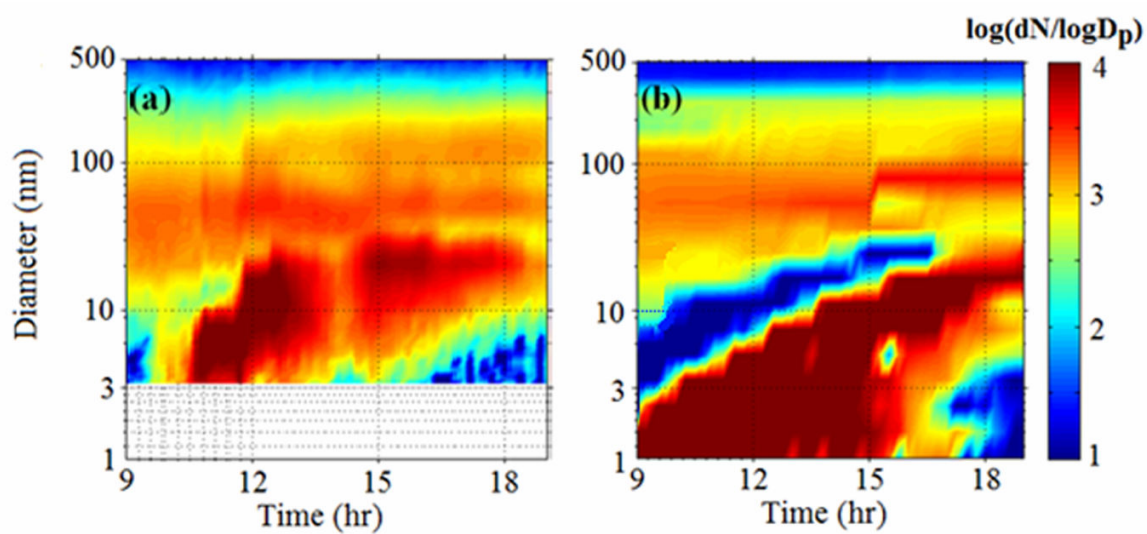
859
860
861
862

863
864
865
866
867
868
869
870
871
872
873
874
875
876
877



878
879 **FIGURE 2:** Simulation with surface tension $\sigma=0.025 \text{ N m}^{-1}$ at Hyytiala: a) predicted particle
880 size distribution with number concentration plotted against time of day (x-axis) and particle
881 diameter (y-axis) and b) the composition of new particles.
882
883
884

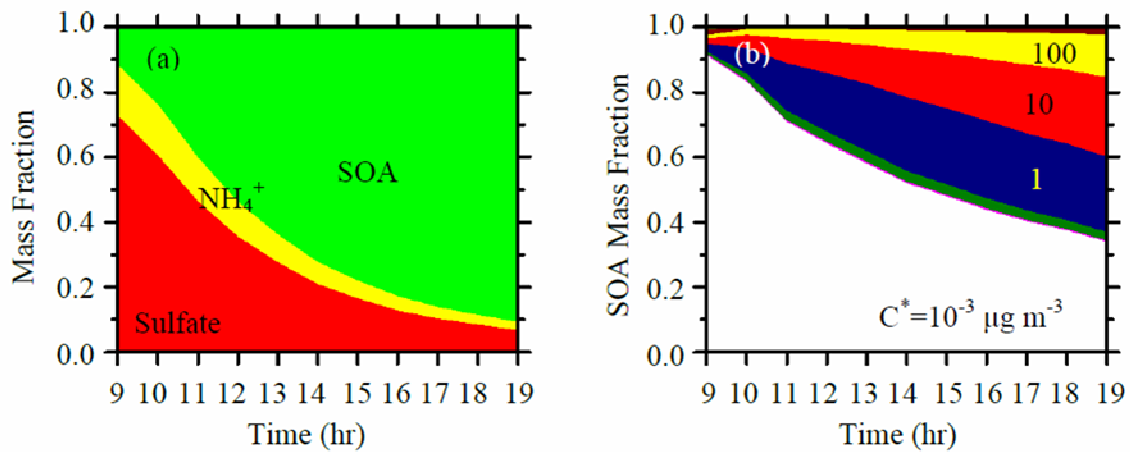
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899



900
901 **FIGURE 3:** Comparison of (a) measured on 10 April 2007 and (b) predicted (with aging of
902 bSOA precursors and $\sigma=0.025 \text{ N m}^{-1}$) dry size distribution as a function of local time at Hyytiala
903 for a typical nucleation event day.

904
905
906

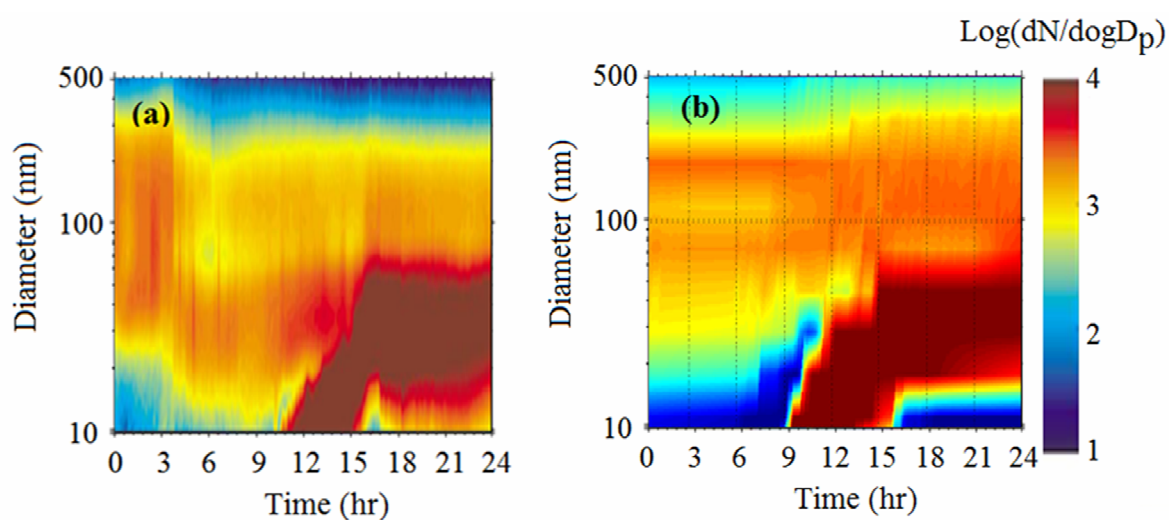
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922



923
924 **FIGURE 4:** a) Mass fraction of fresh particles and b) mass fraction of SOA for the different
925 volatility bins as a function of local time at Hyytiala. Simulation includes bSOA aging and
926 $\sigma=0.025 \text{ N m}^{-1}$.

927
928
929

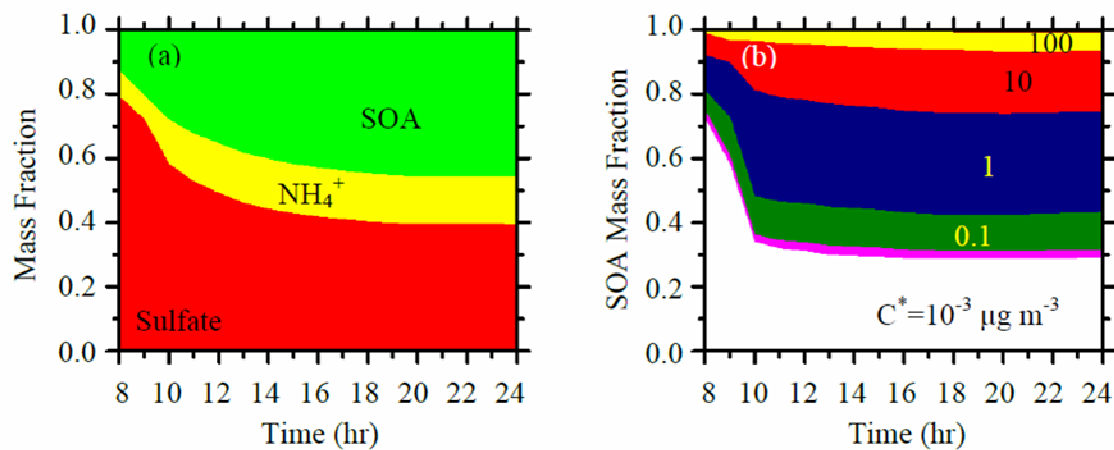
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944



945
946 **FIGURE 5:** Comparison of (a) measured on 19 March 2009 (Pikridas et al., 2012) and (b)
947 predicted dry size aerosol distribution (with bSOA aging and $\sigma=0.025 \text{ N m}^{-1}$) as a function of
948 time at Finokalia.

949
950
951

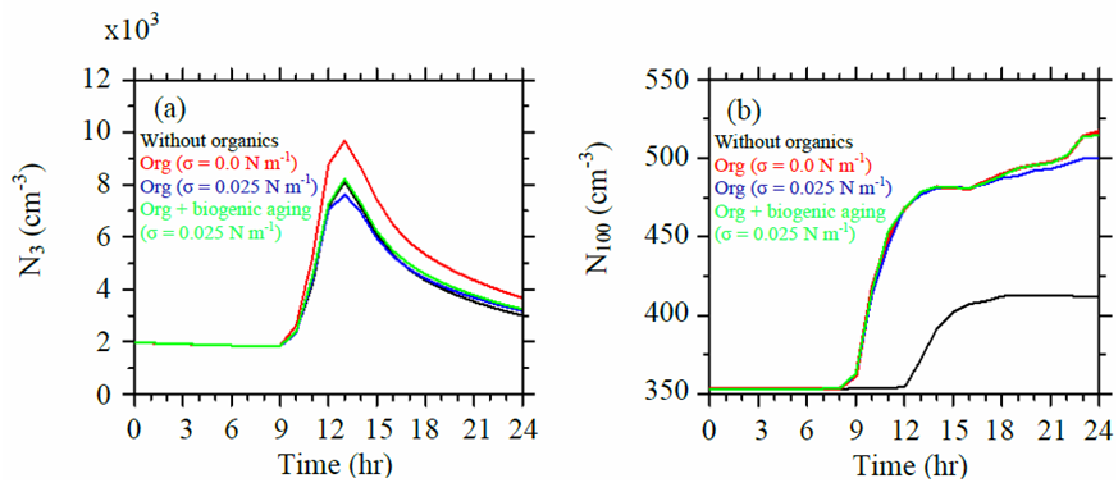
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967



968
969
970
971
972
973
974

FIGURE 6: a) Mass fraction of fresh particles and b) mass fraction of SOA for the different volatility bins as a function of local time at Finokalia. Simulation includes bSOA aging and $\sigma=0.025 \text{ N m}^{-1}$.

975
976
977
978
979
980
981
982
983
984
985
986
987
988
989



990
991 **FIGURE 7:** Predicted concentrations of a) N_3 and b) N_{100} at Hyytiala for the four simulated
992 cases. Black line represents no condensation of organics, red is with condensation of organics
993 with $\sigma = 0.0 \text{ N m}^{-1}$, blue is with condensation of organics with $\sigma = 0.025 \text{ N m}^{-1}$ and green is
994 condensation of organics with aging reactions of bSOA precursors and $\sigma=0.025 \text{ N m}^{-1}$.
995
997