Simulation of the atmospheric life of ultrafine particles

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To my parents, and my brothers
Acknowledgments

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Abstract

The Dynamic Model for Aerosol Nucleation (DMAN) is a model which simulates nucleation, gas-phase chemistry, coagulation and condensation/evaporation for a multi-component atmospheric aerosol population. We developed an updated version of DMAN which includes the condensation of organic vapors on nanoparticles, using the recently developed Volatility Basis Set framework, and simulates the gas phase chemistry using the chemical mechanism SAPRC-99. The simulations were performed for two locations with different organic sources; Hyytiala (Finland) and Finokalia (Greece). Initially, we compared the results of the extended DMAN model with the old version which does not include the condensation of organics. The condensation of organics neglecting the Kelvin effects resulting in an approximate doubling of the growth rate of new particles. The number predicted concentration of particles above 3 nm (N₃) and 100 (N₁₀₀) increased at both locations. The increase of surface tension decreased dramatically the growth rate and the diameter that the new particles reached. The predicted concentration of N₁₀₀ decreased at Hyytiala but increased at Finokalia, while the concentration of N₃ decreased in both locations.

Condensation of semi-volatile organic vapors, assuming realistic values of the organic surface energy, cannot explain the observed growth rates in Hyytiala during typical nucleation events. The simulations with production and condensation of low-volatility organics and a surface tension of 0.025 N m⁻¹ indicate that the model can reproduce well the field measurements. The addition of chemical aging reactions converting semi-volatile organic aerosol (OA) to low volatility compounds helped the model to better reproduce the observed growth of the fresh particles. At Hyytiala, the organics are the major components during the growth process of new particles. The low-volatility secondary OA helps the growth initially, but after a few hours most of the growth is due to semi-volatile secondary OA components. At Finokalia, the simulation shows that the organic components have a complementary role for the growth contributing 45% of the total mass of new particles.
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Chapter 1

Introduction
1.1 Atmospheric ultrafine particles

New particles are introduced in the atmosphere by direct emission from a variety of sources (primary) and nucleation (in situ formation). Primary particles originate from both anthropogenic and natural sources. Secondary particles are formed through nucleation and condensation of gas-phase species significantly influencing the size distribution and number concentrations of atmospheric aerosols (Kulmala et al., 2001; 2004; Stanier et al., 2004). The nucleation and subsequent growth of new particles observed often in various parts of the globe (Kulmala et al., 2004) are important sources of aerosol. These fresh particles formed by nucleation can either grow through the condensation of vapors (e.g. sulfuric acid and ammonia, organics) to larger sizes or can collide with pre-existing aerosols by coagulation and can be lost. Particles smaller than 100 nm are defined as nanoparticles or ultrafine particles. Ultrafine particles have important effects on climate and human health. The new nucleated particles which manage to survive by coagulation can grow to larger size and become cloud condensation nuclei (CCN) affecting the cloud droplet number (Adams and Seinfeld, 2003). The change of cloud condensation nuclei (CCN) concentration affects cloud optical properties and lifetime, perturbing the energy balance of the planet (Twomey 1974; 1977; 1991; Albrecht, 1989). An increase of the number concentration of particles which act as CCN (relevant particle sizes of ~ 100 nm), result in higher cloud droplet number concentrations and to brighter clouds with longer lifetimes. The measurements of CCN at a non-urban site in Germany suggested that CCN concentrations are mainly determined by the aerosol number size distribution and the composition of aerosol plays a secondary role (Dosek et al., 2006). The indirect aerosol radiative forcing is defined as the effect of anthropogenic aerosol on the planet’s radiative balance due to changes on cloud reflectance. The Intergovernmental Panel on Climate Change (IPCC) has estimated a global indirect aerosol radiative forcing of -0.7 W m$^{-2}$, as compared with 2.5 W m$^{-2}$ imposed by change in greenhouse gases (IPCC, 2007). This estimate includes only the effects of aerosol on cloud brightness and neglects the potential increase in cloud lifetimes and the assessed level of scientific understanding is low (IPCC, 2007).

Nanoparticles impact human health by deposition in the human lungs or even brain. This depends on particles size (Peter et al., 1997) and can cause more damage due to the larger surface area per unit mass (Donaldson et al, 1998; 2002). The effects of aerosol composition on health are still uncertain but the composition may be important (Godleski et al., 2000).
Nucleation and subsequent growth by condensation can be important sources of CCN in many parts of the atmosphere (Lihavainen et al., 2003; Kerminen et al., 2005; Laaksonen et al., 2005; Merikanto et al., 2009; Makkonen et al., 2009; Pierce and Adams, 2009; Spracklen et al., 2010; Wang and Penner, 2009; Yu and Luo, 2009). Several mechanisms have been proposed to explain the in-situ particle formation. These include sulfuric acid–water binary nucleation (Nilsson and Kulmala, 1998; Vehkamaki et al., 2002), ternary nucleation (Coffman and Hegg 1995; Korhonen et al., 1999; Kulmala et al., 2002; Napari et al., 2002), nucleation of organic vapors (Marti et al., 1997; Zhang et al., 2004b), ion-induced nucleation (Laakso et al., 2002) and halogen-oxide nucleation (Hoffmann et al., 2001). The binary nucleation mechanism has been the most commonly used with the critical cluster assumed to be composed of H2O and H2SO4. Ternary nucleation theory usually includes ammonia (NH3) as a third component. It is possible that other compounds (e.g. organics, amines) may play a similar role under certain conditions (Bonn et al., 2008; Kurten et al., 2008; Metzger et al., 2010; Smith et al., 2010; Zhao et al., 2011; Berndt et al., 2010; Kirkby et al., 2011). A strong correlation has been found between measured aerosol nucleation rate and the gas-phase sulfuric acid concentration (Weber et al., 1996; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; Nieminen et al., 2009; Paasonen et al., 2009; 2010) in various sites over Europe and the United States. The simulations of nucleation events observed in sulfur-rich regions like the northeastern US appear to be initiated by the formation of gas-phase H2SO4 via SO2 oxidation but terminated by the exhaustion of gas-phase NH3 with ternary sulfate-water-ammonia nucleation appearing to control nucleation (Jung et al., 2008). Some laboratory experiments (Sipila et al., 2010) have revealed a linear or squared correlation between new particle formation rate and concentration of sulfuric acid.

Significant uncertainties arise from the lack of understanding of the identity of the species involved in the formation and growth of these nuclei (Kulmala et al., 2004). Field measurements (Eisele and McMurry, 1997; Weber et al., 1998, 1999; Janson et al., 2001) and model simulations (Kerminen et al., 2001; Kulmala et al., 2000; Pirjola and Kulmala, 2001; Anttila and Kerminen, 2003) indicated that only the condensation of sulfuric acid is often not enough to grow these nuclei to detectable sizes because these fresh particles have a short lifetime due to coagulation with larger particles. Sulfuric acid plays a dominant role in the formation of new particles in the atmosphere by nucleation (Sipila et al., 2010) but it can only explain a small fraction of the particles growth (Riipinen et al., 2010), the rest may be due to organics or other
compounds. The growth of fresh nuclei could be due to the condensation of organic species (Kerminen et al., 2000; Anttila and Kerminen, 2003), heterogeneous reactions (Zhang and Wexler, 2002), or ion-enhanced condensation (Laakso et al., 2002).

1.2 Growth of ultrafine particles

Secondary organic compounds account for a significant mass fraction (20-90%) of submicrometer particulate matter at many locations around the globe and are one of the dominant particle components in the atmosphere (Jimenez et al., 2009). The sources and the chemical composition of organic aerosol (OA) are still uncertain due to the large number (tens of thousands) of different atmospheric organic compounds (Goldstein and Galbally, 2007). OA has been the subject of numerous studies during the last decade (Hallquist et al., 2009). Despite these studies, the properties of organics (e.g., volatility) are still uncertain. Organic aerosol composition continuously evolves with time due to chemical reactions (Kanakidou et al., 2005). Gas-phase oxidation of volatile organic compounds (VOCs) produces semi-volatile products that can then condense to the particle phase. These reactions can be represented by:

\[
VOC_j \xrightarrow{\text{oxidation}} a_{j,1} P_{j,1} + a_{j,2} P_{j,2} + \cdots + a_{j,n} P_{j,n}
\]  

(1.1)

where \( P_{j,i} \) are the products of the oxidation of \( VOC_j \) and \( a_{j,i} \) the corresponding stoichiometric yields.

Most chemical transport models (CTMs) until recently described secondary OA formation using two surrogate species per VOC (one of high and one of low volatility). This approach is computationally expensive due to the large number of products that need to be simulated for all the possible precursors. More importantly, the use of only two products limits the concentration range and the accuracy of this approach. SOA vapors may undergo further gas-phase oxidation and simulation of this aging process would require introduction of even more species (Ng et al., 2006). So a new approach was proposed to address these problems. The Volatility Basic Set framework (Donahue et al., 2006) describes the complete volatility range of OA compounds using logarithmically spaced bins, characterized by an effective saturation concentration, \( C^* \) (in \( \mu g \, m^{-3} \)). The gas phase SOA vapor oxidation can be represented by shifting
mass from high to lower volatility bins. This framework has been shown to work well for simulations of aerosol mass distributions in 3-D CTMs (Lane et al., 2008; Murphy et al., 2009).

**FIGURE 1.1** Mass fraction of OA emissions plotted with using the *Volatility Basic Set* framework (VBS) in terms of \( C^* \) (effective saturation concentration). These bars reveal the volatility distribution of traditionally assumed nonvolatile emissions (Robinson et al., 2007).

Jung et al. (2010) developed a three-dimensional regional CTM with detailed aerosol microphysics, PMCAMx-UF (Gaydos et al., 2007; Karydis et al., 2007). PMCAMx-UF has been used for simulations over Europe for the May period. The model predictions were compared against measurements from seven sites (Fountoukis et al., 2012). The model underpredicted the growth rates, with smaller errors in sites where the sulfate concentration is higher than that of the organics mass (e.g., Melpitz). PMCAMx-UF also underpredicted the number concentration of particles with diameters above 100 nm (\( N_{100} \), the number of particles that can act as CCN) possibly because of insufficient organic vapor condensation (Fountoukis et al., 2012). PMCAMx-UF does not include SOA condensation on ultrafine particles and uses an older gas-phase mechanism (Carbon Bond-IV) which is not compatible with the current treatment of organics (Volatility Basis Set) in PMCAMx-2008 (Fountoukis et al., 2011). Yu (2011) and Riipinen et al. (2010) studied the condensation of organics on ultrafine particles using global CTMs. Yu (2011) estimated that low volatility organics concentration is a factor of 2-20 higher
than H$_2$SO$_4$ over many locations of the continents and can significantly enhance the growth rate of new nucleated particles. He compared predicted particle size distributions with field measurements in a boreal forest site (Hyytiala, Finland) showing that the condensation of low volatility organics can bring the simulation results closer to the observations. Riipinen et al. (2011) found that roughly half of the mass of the condensing mass needs to be distributed proportionally to the aerosol surface area to explain the observed aerosol growth. These compounds need to have very low volatility and this is not compatible with the first generation yields of SOA from biogenic precursors observed in the laboratory. Pierce et al. (2011) found that the average saturation concentrations (C$^*$) of condensing organics need to be around $10^{-3} - 10^{-2}$ μg m$^{-3}$ or less to facilitate the growth of freshly nucleated particles starting at a diameter of 3 nm. The condensation of low volatility organics may play an important role in the growth process of new particles in the atmosphere.

The driving force for condensation of a vapor to an aerosol particle is the difference between its ambient vapor partial pressure and the equilibrium vapor pressure over the particles, or:

$$
\Delta p_i = P_i - P^*_i x_i(D_p) \exp \left( \frac{4 \sigma M}{RT \rho D_p} \right)
$$

where $\Delta p_i$ is the condensational driving force of the organic vapor $i$ (the difference between the gas phase concentration and the effective saturation concentration), $P_i$ is the partial pressure and $x_i$ is the mass fraction of the organic vapor $i$, $P^*_i$ is the saturation pressure of the organic vapor over a flat surface and $\sigma$ is the surface tension, $M$ is the molecular weight of organic vapor, $R$ is the ideal gas constant, $T$ is the temperature, $\rho$ is the liquid-phase density of $i$, and $D_p$ is the diameter of the particle. The exponential term is known as the Kelvin effect due to the curvature of the particles.

The Kelvin equation provides a thermodynamic description for the dependence of the saturation vapor pressure over a particle. The equilibrium pressure increases with decreasing particle size, representing a large limitation for the growth of freshly nucleated particles. Since the Kelvin effect reduces the equilibrium concentrations of organic compounds in the particle phase, it inhibits the growth of nanoparticles by condensation of semi-volatile organic compounds (Zhang et al., 2011). The dominant role of the Kelvin effect for these small particles
suggests that nuclei growth requires the condensation of organic compounds of extremely low volatility (Zhang and Wexler, 2002).

1.3 Objectives and motivation

The overall objective of this work is to examine the contribution of organic vapor condensation to the growth of fresh particles formed by nucleation. We extend the Dynamic Model for Aerosol Nucleation (DMAN) of Jung et al. (2006) which originally assumed that particles grow only by condensation of sulfuric acid and ammonia and by coagulation. In this work, we develop an updated version of DMAN which includes the condensation of organic vapors on particles, using the chemical mechanism SAPRC-99 for the gas phase and the most recent version of the Volatility Basis Set framework. We simulate for the first time the role of the chemical aging reactions of organic aerosol components in the ultrafine particle growth. We examine the effects of condensation of organics, the chemical aging reactions, and the Kelvin effect on the predicted particle number concentrations. We focus on the composition of fresh particles during nucleation events and subsequent growth in two remote continental locations, Hyytiala, Finland and Finokalia, Greece where there are comprehensive measurements available to constrain the model. This is the first step for improving the predictions of PMCAMx-UF.
Chapter 2

Model Description
2.1 DMAN model

The Dynamic Model for Aerosol Nucleation (DMAN) (Jung et al., 2006) simulates nucleation, gas phase chemistry, coagulation and condensation/evaporation for a multi-component atmospheric aerosol population. It can be used as a module in a three-dimensional CTM such as PMCAMx-UF (Jung et al., 2010). DMAN uses the Two-Moment Aerosol Sectional (TOMAS) algorithm of Adams and Seinfeld (2002) which is based on the sectional approach for the description of the aerosol size composition distribution. The TOMAS algorithm is an adaptation of cloud microphysics algorithms (Tzivion et al., 1987; 1989) to aerosol processes, it is computationally efficient, and tracks both mass and number concentrations simultaneously. The use of mass as a variable is convenient for coagulation simulations because it is conserved and also allows the direct transformation of the number to the mass distribution (Tzivion et al., 1987; 1989). The aerosol size distribution is described with 41 size sections with the lowest boundary at $3.75 \times 10^{-25}$ kg dry aerosol mass per particle. That corresponds to 0.8 nm dry diameter assuming a density of 1.4 g cm$^{-3}$. Each successive boundary has double the mass of the previous one. The largest bin corresponds to about 10 μm.

2.2 Nucleation

The rate of nucleation is calculated using the ternary nucleation parameterization of Napari et al. (2002) if the NH$_3$ concentration exceeds 0.01 ppt and the binary parameterization of Vehkamaki et al. (2002) if it is less than this threshold value. The ternary NH$_3$-H$_2$SO$_4$-H$_2$O nucleation model is successful in predicting the presence or lack of nucleation (Gaydos et al., 2005). However, the ternary original nucleation parameterization (Napari et al., 2002) seems to overpredict ultrafine number concentrations during nucleation events (Gaydos et al., 2005; Yu, 2006a, b; Jung et al., 2006; 2008; Merikanto et al., 2007; Zhang et al., 2010) and thus a scaling factor of $10^{-5}$ is applied in the work to the nucleation rate following Jung et al. (2010). The critical nucleus is predicted to consist of roughly two molecules of sulfuric acid and two molecules of ammonia (Napari et al., 2002), so it is assumed that the nucleated particles are NH$_4$HSO$_4$. 


2.3 Gas-phase chemistry

In this work, the simulation of gas phase chemistry in DMAN is updated into DMAN model using the SAPRC99 chemical mechanism (Carter, 2000; Environ, 2003). This chemical mechanism includes 211 reactions of 56 gases and 18 free radicals and also includes five lumped alkanes, two lumped olefins, two lumped aromatics, isoprene, a lumped monoterpene, and a lumped sesquiterpene species. Only the two highest molecular weight alkane species are considered volatile organic aerosol precursors because the other three consist of smaller hydrocarbons (Pandis et al., 1991). OLE1 contains all the terminal alkenes, while OLE2 consists of all the internal alkenes and cyclic alkenes. The major compounds for each VOC class which are used in SAPRC99 are listed in Table 2.1 (Tsimpidi et al., 2010). The nine lumped VOCs are considered as volatile SOA precursors with three of them being biogenic and the rest anthropogenic.

### TABLE 2.1 Major compounds for each lumped VOC within SAPRC99 (Tsimpidi et al., 2010).

<table>
<thead>
<tr>
<th>Species</th>
<th>Major Components</th>
<th>Type of source</th>
<th>V-SOA precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALK1</td>
<td>Ethane, Methyl Formate</td>
<td>Anthropogenic</td>
<td>No</td>
</tr>
<tr>
<td>ALK2</td>
<td>Propane, Cyclobutane, Ethyl Formate, Methyl Acetate</td>
<td>Anthropogenic</td>
<td>No</td>
</tr>
<tr>
<td>ALK3</td>
<td>n-Butane, Ethanol, Isobutane, Dimethyl, Butane, Dimethyl Pentane</td>
<td>Anthropogenic</td>
<td>No</td>
</tr>
<tr>
<td>ALK4</td>
<td>n-Pentane, n-Hexane, Branched C5-C6, Alkanes, Cyclopetane, Trimethyl Butane, Trimethyl Pentane, Isopropyl Alcohol, n-Propyl Alcohol</td>
<td>Anthropogenic</td>
<td>Yes</td>
</tr>
<tr>
<td>ALK5</td>
<td>C7-C22 n-Alkanes, C6-C16 Cycloalkanes, Branched/Unspeciated C8-C18 Alkanes</td>
<td>Anthropogenic</td>
<td>Yes</td>
</tr>
<tr>
<td>OLE1</td>
<td>Propene, C4-C15 Terminal Alkenes</td>
<td>Anthropogenic</td>
<td>Yes</td>
</tr>
<tr>
<td>OLE2</td>
<td>Isobutene, C4-C15 Internal Alkenes, C6-C15 Cyclic or di-olefins, Styrenes</td>
<td>Anthropogenic</td>
<td>Yes</td>
</tr>
<tr>
<td>ARO1</td>
<td>Toluene, Benzene, Ethyl Benzene, C9-C13 Monosubstituted Benzenes</td>
<td>Anthropogenic</td>
<td>Yes</td>
</tr>
<tr>
<td>ARO2</td>
<td>Xylenes, Ethyl Toluens, Dimethyl and Trimethyl Benzenes, Ethylbenzenes, Naphthalene, C8-C13 Di-, Tri-, Tetra-,Penta-, Hexa-substituted Benzenes, Unspeciated C10-C12 Aromatics</td>
<td>Anthropogenic</td>
<td>Yes</td>
</tr>
<tr>
<td>TERP</td>
<td>α-pinene, β-pinene, Limonene, Carene, Sabinene, other monoterpene</td>
<td>Biogenic</td>
<td>Yes</td>
</tr>
<tr>
<td>ISOP</td>
<td>Isoprene</td>
<td>Biogenic</td>
<td>Yes</td>
</tr>
<tr>
<td>SESQ</td>
<td>Sesquiterpenes</td>
<td>Biogenic</td>
<td>Yes</td>
</tr>
</tbody>
</table>
2.4 Coagulation

Coagulation of particles in the atmosphere is an important sink of aerosol number but it is also a mechanism by which freshly nucleated particles grow to larger sizes. The TOMAS algorithm is used for the simulation of coagulation. The portion of the aerosol general dynamic equation relating to coagulation (known also as the stochastic collection equation) is solved using the method of the two moments following equations of Adams and Seinfeld, (2002):

\[
\frac{dN_k}{dt} = \frac{1}{2} K_{k,k+1} N_{k+1}^2 - K_{k,k} N_k^2 - N_k \sum_{i=k+1}^{l} K_{k,i} N_i + \sum_{i=1}^{k-1} K_{k-1,i} M_i - \psi_k \sum_{i=1}^{k-1} K_{k,i} M_i + \frac{\psi_k + f_k}{2x_k} \xi \sum_{i=1}^{k-1} K_{k,i} M_i - \frac{\psi_k - f_k}{2x_k} \xi^3 \sum_{i=1}^{k-2} K_{k-1,i} M_i m_i^2
\]

(2.1)

\[
\frac{dM_k}{dt} = K_{k,k+1} N_{k+1} M_{k+1} - K_{k,k} N_k M_k + N_k \sum_{i=k+1}^{l} K_{k,i} M_i - M_k \sum_{i=k+1}^{l} K_{k,i} N_i + \frac{\psi_k + f_k}{2x_k} \xi \sum_{i=1}^{k-1} K_{k,i} M_i + \frac{\psi_k - f_k}{2x_k} \xi^3 \sum_{i=1}^{k-2} K_{k-1,i} M_i m_i^2
\]

(2.2)

where \(N_k\) and \(M_k\) are the total number and mass of aerosol particles in the \(k\)-th size section, \(x\) depends on the bin spacing and is equal to 1.0625 for the mass-doubling used, \(K_{j,k}\) is the coagulation coefficient for particles in the \(j\)-th bin with particles in the \(k\)-th, \(f_k\) and \(y_k\) are parameters that describe the linear approximation to the number distribution that are defined in Tzivion et al. (1987), \(x_k\) is the lower boundary of the \(k\)-th size bin in terms of dry mass, \(m_k\) is the average mass of particles in the \(k\)-th bin, and \(i\) is the total number of size bins. It is assumed that the aerosol particles coagulate via Brownian diffusion and the effects of gravitational settling and turbulence are negligible. The calculation of the coagulation coefficients is based on the wet diameters of the particles. These wet diameters are calculated following the approach of Gaydos et al. (2005). The coagulation kernel, \(K_{j,k}\) is recalculated at every grid cell and time step to take into account changes in particle size due to humidity changes. The Stokes-Einstein formula has been used to calculate the diffusivities of aerosol particles (Adams and Seinfeld, 2002). For small particles (<100 nm), we use the expression of Dahneke et al. (1983) in order to correct for non-continuum effects. The coagulation algorithm uses an adaptive time step. The time step is limited
so that the aerosol number or mass concentration in any size category does not increase by more than an order of magnitude or decreases by more than 25%.

2.5 Condensation

Condensation of gas-phase species to existing aerosol particles is an important source of aerosol mass and a means by which small particles grow to CCN size. The TOMAS algorithm is used for the simulation of condensation/evaporation of sulfuric acid, ammonia and organic vapors.

2.5.1 Condensation of organic vapors

The TOMAS algorithm (Adams and Seinfeld, 2002) is used for the description of the condensation of organic vapors using the wet diameters of the particles (Gaydos et al., 2005). The driving force for condensation is the difference between bulk partial pressure and equilibrium vapor pressure. The parameter $\tau$ describes the driving force for condensation in TOMAS (see Adams and Seinfeld, 2002 for a detailed derivation).

$$\tau = \frac{2\pi DM}{RT} \sqrt[3]{\frac{6}{\pi \rho_k}} F(Kn,a) \int_{t}^{t+\Delta t} \Delta p(t) dt \quad (2.3)$$

where $D$ is the diffusivity of organic vapors in air, $M$ is their molecular weight, $R$ is the ideal gas constant, $\rho_k$ is the density of aerosol in size bin $k$, and $F$ is a correction factor for non-continuum effects. $F$ is a function of $Kn$, the Knudsen number and $a$, the accommodation coefficient which is calculated using the expression proposed by Dahneke et al. (1983). We have chosen a value of 1 for the accommodation coefficient of organic vapors. The quantity $\Delta p$ is the difference between the partial pressure of condensing vapor and its equilibrium vapor pressure (Eq. 1.2). In Eq. 1.2, the Kelvin effect depends largely in the particle diameter $D_p$ and the surface tension $\sigma$. The exponential term includes the diameter in the denominator, therefore, for small particles the exponential term is large and prevents the condensation of organic vapors on small particles. The Kelvin effect is very important for the behavior and growth of small particles.

We also use an adaptive time step to efficiently solve the equations for condensation. The time step is chosen so that individual particles in any size bin do not grow by more than 10%, the partial pressure of the organic vapor does not fall below 25% of its original value, and is never longer than 15 min.
2.5.2 Condensation of sulfuric acid

Sulfuric acid is assumed to be in pseudo steady state in our model. The previous version of DMAN used a fourth-order Runge-Kutta and an adaptive time step (Press et al., 1992) for the integration of the corresponding differential equations. This numerical approach is accurate but it requires significant computational time. The Pseudo-Steady-State Approximation (PSSA) for sulfuric acid proposed by Pierce and Adams (2009) increases the computational speed with a small loss in accuracy. Sulfuric acid vapor is consumed by condensation onto pre-existing particles and nucleation and is produced by the reaction of SO$_2$ with OH. The PSSA assumes that sulfuric acid concentration reaches steady state instantaneously during a time step. The resulting equation is:

$$\frac{d[H_2SO_4]_{SS}}{dt} = P_{H_2SO_4} - CS \cdot [H_2SO_4]_{SS} - J_{nuc}M_{nuc}$$

(2.4)

where $P_{H_2SO_4}$ is the chemical production rate of sulfuric acid vapor, $CS$ is the condensation sink (first-order condensational loss rate constant) for sulfuric acid vapor, $[H_2SO_4]_{SS}$ is the steady state concentration for sulfuric acid vapor, $J_{nuc}$ is the nucleation rate, and $M_{nuc}$ is the amount of sulfuric acid in each nucleating particle.

The PSSA method was tested for a variety of conditions ranging from highly polluted to extremely clean conditions. Its predictions for the sulfuric acid vapor concentration and the number of new particles formed during typical atmospheric nucleation events agree very well with the “benchmark model” (Pierce and Adams, 2009). Jung et al. (2010) evaluated the performance of PSSA for sulfuric acid in DMAN against a 4th order Runge-Kutta algorithm and showed that PSSA is accurate and computationally efficient.

2.5.3 Condensation of ammonia

Condensation of ammonia is simulated following the approach described by Jung et al. (2006). Ammonia condensation ends when the sulfate in the aerosol is fully neutralized to ammonium sulfate. The equilibrium ammonia vapor pressure is assumed to be zero when aerosols are acidic, i.e. molar ratio of NH$_4^+$ and SO$_4^{2-}$ is <2. If the amount of condensed ammonia exceeds the amount needed to neutralize particles during a time step, we limit the maximum amount of ammonia that can condense. We define the maximum $\tau$ for ammonia
condensation as $\tau_{\text{max}}$ and the maximum amount of ammonium in the particles of size section $k$ as $M_{k,NH_4}^{\text{max}}$.

$$M_{k,NH_4}^{\text{max}} = \frac{2m_{NH_4}}{m_{SO_4}} M_{k,SO_4}$$  \hspace{1cm} (2.4)

$$\tau_{\text{max}} = \frac{1.5\left(M_{k,NH_4}^{\text{max} \cdot \frac{1}{2}} - M_{k,NH_4}^{\cdot \frac{1}{2}}\right)}{N_k^{\cdot \frac{1}{2}}}$$  \hspace{1cm} (2.5)

where $m_{NH_4}$ and $m_{SO_4}$ are the molecular weights of ammonium and sulfate respectively, $M_{k,NH_4}$ and $M_{k,SO_4}$ are the sulfate and ammonium mass in size bin $k$, and $N_k$ is the number in the $k$-th size bin.

### 2.6 Secondary organic aerosol formation from VOCs

The model framework is based on the Volatility Basic Set (VBS) (Donahue et al., 2006; Lane et al., 2008a). SOA components partition between the aerosol and gas phases, and can be formed from anthropogenic (aSOA) and biogenic (bSOA) precursors. Each of these types is simulated with 12 volatility bins ($10^{-5} - 10^6 \mu g m^{-3}$). We assume, for both aSOA and bSOA, average molecular weights of 200 g mol$^{-1}$ and that the effective enthalpies of vaporization are 30 kJ mol$^{-1}$ (Pathak et al., 2007; Stanier et al., 2007). The SOA yields used in the updated version of DMAN are based on the NO$_x$-dependent stoichiometric yields of Lane et al. (2008a). The anthropogenic yields for the low NO$_x$ case are in general higher than in the high NO$_x$ case (Lane et al., 2008a). Recent laboratory studies have shown that the aromatic VOC SOA yields are higher than originally thought (Ng et al., 2006; Hildebrandt et al., 2009). The SOA yields in this work are calculated by multiplying the experimentally determined yields, based on aerosol volume concentration, by 1.5 (Murphy et al., 2009) using an average SOA density of 1.5 g cm$^{-3}$ (Kostenidou et al., 2007).

Organic products with high vapor pressure can be oxidized to species with lower volatility (Donahue et al., 2006) leading to SOA production. The chemical aging of semi-volatile organic vapors is modeled using a second order reaction with hydroxyl radical. We assume that each aging chemical reaction reduces the volatility of the corresponding organic vapor by one order of magnitude (i.e. shifting organic material from a saturation concentration $C^*$ of e.g. $10^3$ to
10^2 \mu g m^{-3}), with a small net increase in mass (7.5\%) to account for the added oxygen. The chemical reactions for anthropogenic sources (aSOA) are modeled with a rate constant \( k (298 \text{ K}) = 1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) (Murphy et al., 2009). The aSOA aging is based on OH oxidation of the products of aromatic VOC oxidation (Atkinson et al. 2000; 2003). In the base case, the aging of biogenic SOA is assumed to have a negligible effect on OA concentration, this assumption is based both on the laboratory studies (Ng et al., 2006; Presto et al., 2006) and on the work of Lane et al. (2008).

In this work, we added a reaction converting the gas-phase fraction of the \( C^* = 1 \mu g m^{-3} \) material to low volatility biogenic SOA with \( C^* = 10^{-3} \mu g m^{-3} \) with a reasonable rate constant (1 x 10^{-11} cm^3 molec^{-1} s^{-1}). The importance of this hypothesized pathway of formation of extremely low volatility organic material for the growth of newly formed particles will be explored in a subsequent section.

2.7 Model Application

Initially, the extended DMAN was tested in Hyytiala (Finland). Meteorological data, gas-phase concentrations, and aerosol number concentrations are available as inputs from ground-level measurements at the SMEAR II station in Hyytiala. SMEAR II (Station for Measuring Forest Ecosystem–Atmosphere Relations) is located in a rather homogenous Scots pine (Pinus sylvestris) stand on flat terrain at the Hyytiala Forestry Field Station of the University of Helsinki (61°51'N, 24°17'E, 181 m above sea level). The biggest city near SMEAR II is Tampere which has about 200,000 inhabitants and is located about 60 km from the measurement site. Hari and Kulmala (2005) have described the station and its operation in detail. The main inputs of our simulations are meteorological data (temperature and relative humidity), \( \text{SO}_2 \), \( \text{NH}_3 \), OH, \( \text{O}_3 \) and VOC concentrations and initial aerosol number distribution. The \( \text{SO}_2 \), \( \text{O}_3 \) concentration, T and RH were measured continuously. The OH concentration was based on the predictions of the 3-D model PMCAMx-2008 (Fountoukis et al., 2011). For lumped VOCs, the concentration of TERP, ISOP, ARO1 were estimated based on the 3 hour averages of the Proton Transfer Reaction Mass Spectrometer (PTRMS) measurements. A detailed description of the PTR-MS technique is given by Lindinger et al. (1998a; b). The rest of the lumped VOCs were estimated from the predictions of PMCAMx-2008. The concentration of \( \text{NH}_3 \) was based on the measurements during the QUEST IV campaign in Hyytiala (Riipinen et al., 2007). The initial aerosol number distributions
are available from ambient dry size distributions which were measured every 15 min using a Differential Mobility Particle Sizer (DMPS). A detailed description of the DMPS setup applied in Hyytiala is given by Aalto et al. (2001). In each simulation, we assumed that half of the initial particle mass consists of OM and the other half is ammonium sulfate.

We also tested the new model in Finokalia, a remote area in the Eastern Mediterranean region. This allowed us to examine the role of the condensation of organics in other places with less organics emissions for a typical day with nucleation events. Finokalia (35° 24’ N, 25° 60’ E) is a remote coastal station located in the southeast of the Mediterranean Sea on the island of Crete, Greece. The nearest large urban center is Heraklion with 150,000 inhabitants located 50 km west of Finokalia. The Finokalia station is located at the top of a hill at an elevation of 230 m, facing the sea. There is no notable human activity at a range of approximately 15 km (Kouvarakis et al., 2000). There are very few trees and little vegetation in surrounding area. Most of the aerosol at the site is transported from the surrounding regions, such as Greece, Turkey and northern Africa (Pikridas et al., 2010). The concentrations of NH₃, SO₂ and aerosol number distributions was estimated based on the measurements during the Finokalia Aerosol Measurement Experiment -2008 and -2009 (FAME-08 and FAME-09)(Pikridas et al., 2010; 2012). The other inputs were estimated from the predictions of PMCAMx-2008 (Fountoukis et al., 2011).
Chapter 3

Results
3.1 Effects of condensation of organic vapors

To quantify the effect of the condensation of organic vapors on ultrafine particle growth, we compared the results of the extended DMAN model with those of the Jung et al. (2006) version, i.e. a model simulating the condensation of organics against a model neglecting organic condensation. We simulated a typical spring day with nucleation in Hyytiala, Finland and in Finokalia, Greece. The model simulates a full day beginning at midnight.

3.1.1 Simulation without condensation of organic vapors

In the simulation neglecting the organic contribution to ultrafine particle growth in Hyytiala the new particles reach a diameter of 9 nm and the growth rate is only 1 nm h\(^{-1}\) (Fig. 3.1a). The nucleation event starts at 6:00 and ends at 17:00. A significant advantage of the model is that it can predict the composition of fresh particles formed by nucleation. The growing nucleation mode consists of sulfate and ammonium without any organics (Fig. 3.1b).

FIGURE 3.1 a) Predicted aerosol dry size distribution for a typical spring nucleation event at Hyytiala without organics condensation. Particle number concentration is plotted against time of day (x-axis) and particle diameter (y-axis). b) Predicted composition of new particles.

In the Finokalia nucleation simulation, the model predicted that the fresh particles grew up to 32 nm with a rate of 3 nm h\(^{-1}\) which is less than the 5 nm h\(^{-1}\) reported by Pikridas at el. (2010; 2012). The nucleation started at 7:00 and ended at 15:00. The particles reached a diameter equal to 10 nm at 10:00. These new particles consist of only sulfate and ammonium (Fig 3.2b).
At the start of the nucleation event these consist of 93% sulfate and this fraction drops to 72% at the end of day.

**FIGURE 3.2** a) Predicted aerosol dry size distribution during a typical day with a nucleation event at Finokalia without organics condensation. Particle number concentration is plotted against time of day (x-axis) and particle diameter (y-axis). b) The composition of new particles.

### 3.1.2 Organic condensation neglecting the Kelvin effect

The condensation of organics neglecting the Kelvin effect assuming zero surface energy helps the newly formed particles to reach a diameter of 28 nm in Hyytiala and the average growth rate is 1.8 nm h\(^{-1}\) (Fig. 3.3a). The nucleation event starts at 7:00 and ends at 15:00. At 8:00 the nucleation mode particles have a size around 2 nm and consist of 55% sulfate, 11% ammonium and 34% organics. During the day the new particles continue to grow and the fraction of organics increases to 85% at end of the day (Fig. 3.3b).

The mass concentration of new particles increases due the condensation of organics. The maximum mass concentration of fresh particles is 5.5 ng m\(^{-3}\) at 19:00 (Fig. 3.4a). The surrogate OA components with effective saturation concentration of \(C^* = 1\) and 10 μg m\(^{-3}\) are predicted to be the major components of the fresh particles contributing 80% of the SOA initially and 70% in the end (Fig. 3.4b). These OA components are produced by the oxidation of both biogenic and anthropogenic VOCs.
FIGURE 3.3 Simulation with condensation of organics neglecting the Kelvin effect at Hyytiala: a) the predicted aerosol dry size distribution and b) the composition of nucleated particles.

FIGURE 3.4 Simulation with zero surface energy of OA at Hyytiala: a) the mass concentration of new particles and b) the predicted composition of organic aerosol in the new particles for different effective saturation concentrations.

For the Finokalia case, the predicted growth rate of new particles is 3.8 nm h$^{-1}$ and the diameter of the new fresh particles reaches 42 nm. The condensation of organics helps the particles to grow faster and reach larger sizes. At 8:00 the particles consist of 35% organics, 5% ammonium and 60% sulfate (Fig. 3.5b). After 11:00 the new particles composition is relatively stable: 40% organics, 42% sulfate and 18% ammonium. For this case of zero surface tension organics condense immediately on the newly formed particles and this result in fast growth.
FIGURE 3.5 Simulation with condensation organics neglecting the Kelvin effect at Finokalia as function of time: a) predicted particles size distribution and b) the composition of nucleated particles.

The predicted temporal evolution of the mass concentration in Finokalia is similar to that at Hyytiala with a maximum value of the mass of the nucleation mode of 80 ng m$^{-3}$ at 19:00. The surrogate OA species with C* = 1 and 10 μg m$^{-3}$ were the major components of new particles in this case too representing around 70% of the OA during the day (Fig 3.6b).

FIGURE 3.6 Simulation neglecting surface energy at Finokalia: a) the predicted mass concentration of new particles and b) the predicted composition of organic aerosol in the new particles.
3.1.3 Organic condensation with \( \sigma=0.05 \text{ N m}^{-1} \)

During the simulation with organic vapor condensation assuming that \( \sigma=0.05 \text{ N m}^{-1} \), the predicted growth rate in Hyytiala is only 1.1 nm h\(^{-1}\) and the diameter of new particles in the end of the day is 12 nm (Fig. 3.7a). The increase of surface tension practically prevents the condensation of organics on fresh particles and few particles can grow above the diameter of 3 nm. Surface tension has also a major affect, as expected, on the composition of the new particles. At the beginning of the nucleation event (Fig. 3.7b), the new particles do not contain any organics. Their initial growth is due to the condensation of sulfuric acid and ammonia. At 12:00 when the new particles have reached a diameter of 4 nm, the effect of surface tension has decreased and organics start slowly condensing contributing to growth. The mass fraction of organics in the particles gradually increases reaching 45% at the end of the day (Fig. 3.7b).

![Simulation with surface tension of 0.05 N m\(^{-1}\) at Hyytiala: a) predicted particle size distribution with number concentration plotted against time of day (x-axis) and particle diameter (y-axis) and b) the composition of new particles.](image)

**FIGURE 3.7** Simulation with surface tension of 0.05 N m\(^{-1}\) at Hyytiala: a) predicted particle size distribution with number concentration plotted against time of day (x-axis) and particle diameter (y-axis) and b) the composition of new particles.

The organic composition of the fresh particles in Hyytiala is different compared to the previous cases. The components with lower volatility (\( C^*=10^{-2} \) and \( 10^{-3} \mu\text{g m}^{-3} \)) now contribute around 30% of the organic mass in the initial stages of the growth (Fig. 3.8b). Another 50% is due to the \( C^*=0.1 \) and 1 \( \mu\text{g m}^{-3} \) components. As the day goes on the contribution of the more volatile components increases and at the end of the day 60% of the new particle organic mass is relatively volatile material of 1 and 10 \( \mu\text{g m}^{-3} \). Figure 3.8a shows that the maximum mass concentration of the new particles is only 0.055 ng m\(^{-3}\) in this case.
FIGURE 3.8 Simulation with $\sigma = 0.05 \text{ N m}^{-1}$ at Hyytiala: a) mass concentration of nucleated particles, and b) the predicted composition of organic aerosol in the fresh particles.

In the case of $\sigma = 0.05 \text{ N m}^{-1}$ at Finokalia, the predicted growth rate is 3.7 nm h$^{-1}$ and the new particles’ diameter reaches 40 nm. At 9.30 the particles consist of 90% sulfate, 6% ammonium and 4% organics. The organics condensation accelerates later, as these particles become larger than 3 nm after 10:00. The SOA mass fraction increases to 35% by the end of day.

FIGURE 3.9 Simulation with surface tension of 0.05 N m$^{-1}$ at Finokalia: a) predicted particle size distribution and b) the composition of nucleated particles.

The increase of the surface tension does not change the temporal evolution of the mass concentration of new particles (Fig. 3.10a). However, the mass of particles decreases, compared
to the zero surface energy reaching a maximum value of 62 ng m\(^{-3}\) instead of 80 ng m\(^{-3}\). The composition of the SOA is similar to that of the zero surface tension case (Fig 3.10b).

**FIGURE 3.10** Simulation with \(\sigma = 0.05\) N m\(^{-1}\) at Finokalia: a) the mass concentration of nucleated particles and b) the predicted composition of organic aerosol in the new particles.

### 3.2 Sensitivity of the number concentration to surface tension

The previous results of the model showed that organic condensation can cause a significant increase in the mass concentration of the fresh particles. However, the large particles also grow by organic condensation at the same time resulting in increasing probability of the newly formed particles to collide with large particles and therefore to disappear. This causes a significant reduction in the concentration of small particles. The increase of surface tension leads to organic vapor condensation mostly on large particles and to a smaller extent on freshly nucleated particles.

The predicted daily mean number concentration of particles above 3 nm (\(N_3\)) in Hyytiala is 2,800 cm\(^{-3}\) for the simulation without organics, 8,900 cm\(^{-3}\) when surface tension is zero and 2,600 cm\(^{-3}\) when the organic surface tension is 0.05 N m\(^{-1}\) (Fig. 3.11). The number concentration of particles above 100 nm (\(N_{100}\)) is 360 cm\(^{-3}\) without organics, 470 cm\(^{-3}\) when neglecting the Kelvin effect and 440 cm\(^{-3}\) when the surface tension is 0.05 N m\(^{-1}\) (Fig. 3.11b). Neglecting the Kelvin effect allows rapid condensation of organics on the fresh particles resulting in the increase of \(N_3\) and \(N_{100}\) during the early afternoon. An increase of surface tension practically prevents the condensation of organics on fresh particles and thus fewer particles can grow above the diameter of 3 nm. However, the produced semi-volatile organic vapors condense on the
existing sub-100 nm particles assisting them to grow above 100 nm. By 21:00 the concentration of the particles above 100 nm is similar to that of the case with zero surface tension (Fig. 3.11b).

**FIGURE 3.11** Predicted concentrations of a) N\textsubscript{3} and b) N\textsubscript{100} at Hyytiala for the three simulated cases.

The average predicted daily concentration of N\textsubscript{3} at Finokalia is 4000 cm\textsuperscript{3} without condensation of organics, 6700 cm\textsuperscript{3} for zero surface tension, and 4400 cm\textsuperscript{3} for \(\sigma = 0.05\) N m\textsuperscript{-1} (Fig. 3.12). The concentration of N\textsubscript{100} starts to increase after 10:00 for the case of \(\sigma = 0\) N m\textsuperscript{-1} and \(\sigma = 0.05\) N m\textsuperscript{-1} while after 12:00 for the no-organics case. The number concentration of particles that can act as CCN (N\textsubscript{100}) is 810 cm\textsuperscript{3} without organics, 840 cm\textsuperscript{3} when \(\sigma = 0.05\) N m\textsuperscript{-1} and 900 cm\textsuperscript{3} when \(\sigma = 0.05\) N m\textsuperscript{-1}.

**FIGURE 3.12** Predicted concentrations of a) N\textsubscript{3} and b) N\textsubscript{100} at Finokalia for the three simulated cases.
FIGURE 3.13 The daily average concentration of a) N$_3$ and b) N$_{100}$, for the different values of surface tension of organics for Finokalia (red line) and Hyytiala (black line). The dashed lines represent the results of the simulations without condensation of organics.

Increasing the surface tension for both locations decreases the average daily N$_3$ (Fig. 3.13a). The decrease of N$_3$ at Hyytiala is larger than at Finokalia. For larger values of surface tension (0.025 - 0.07 N m$^{-1}$), organics condense mainly on the larger particles resulting in an increase of the coagulation rate which significantly decreases the number of small particles. For surface tension between 0.035 and 0.07 N m$^{-1}$, N$_3$ in Hyytiala is predicted to be less than in the no-organics simulation. At Finokalia on the other hand, for small value of surface tension, the decrease of N$_3$ is less than in Hyytiala due to the fact that organics have a less important role on the growth of these particles.

Increasing the magnitude of the Kelvin effect decreases the average N$_{100}$ at Hyytiala but increases it at Finokalia (Figure 3.13b). This is because the number size distribution of the pre-existing particles is very different at the two locations. At Finokalia there are more and larger particles than at Hyytiala. Condensation of organics in Hyytiala results in fewer particles that finally manage to grow above 100 nm compared to Finokalia. The contribution of organics to N$_3$ and N$_{100}$ is different in the two places and depends on the number and the size of the pre-existing particles in each place.
3.3 Contribution of extremely low volatility organics to new particle growth

For Hyttiala the model predictions for the new particles growth is consistent with the measurements only when we include the condensation of semi-volatile organics without taking into account the Kelvin effect. However, using a zero value for surface tension is unrealistic. The simulation in Hyttiala with condensation of organics and $\sigma$= 0.025 N m$^{-1}$ (this value of surface tension was used by Pierce et al., (2011)) shows that the new particles can reach a diameter of 10 nm with a small growth rate. Condensation of semi-volatile organics with $\sigma$= 0.025 N m$^{-1}$ (base case) cannot assist the new particles to grow to sizes comparable to the field measurements.

Alternative hypothesis is that condensation of very low volatility organics may explain the observed growth. We assume that a small fraction of organics, which are produced from the oxidation of biogenic VOCs, form very low volatile organics with saturation concentration of $C^*$ = 10$^{-3}$ $\mu$g m$^{-3}$. We examined three cases: 5%, 10% and 15% of the first generation products of the VOC oxidation have an effective saturation concentration of $C^*$ =10$^{-3}$ $\mu$g m$^{-3}$. In the 5% case the predicted growth rate is 2.4 nm h$^{-1}$ while for the other two cases the model predicts a 3.3 nm h$^{-1}$ and 3.7 nm h$^{-1}$ growth rate respectively. The results show that very low-volatility organic condensation on new particles can help them reach higher diameters even if the pre-existing particles grow significantly at the same time (Fig.3.14).

**FIGURE 3.14**  Particles size distribution with condensation of organics and $\sigma$= 0.025 N m$^{-1}$ as a function of time in Hyttiala, a) 5%, b) 10%, and c) 15% of the products of VOC oxidation are assumed to have very low effective volatility ($C^*$ = 10$^{-3}$ $\mu$g m$^{-3}$).
FIGURE 3.15 Predicted new particles composition assuming $\sigma = 0.025 \text{ N m}^{-1}$ for three different yields of extremely low volatility products in Hytiala: The composition of new particles for a) 5% yield, b) 10%, c) 15%, and the predicted composition of organics for d) 5% yield, e) 10% and f) 15%.

At the beginning of particle growth, the low volatility organics dominate the mass of new particles in all cases because these particles are small and the more volatile organics cannot easily condense on such small particles. After these particles grow to diameters above 3-4 nm, the semi-volatile organics start to condense and their mass fraction reaches the maximum value (85% for 5% yield, 75% for 10% and 65% for 15%) at the end of the day (Fig.3.15). The existence of extremely low volatility condensable mass with $C^* = 10^{-3} \mu \text{g m}^{-3}$ tends to considerably increase the total OA concentration. The average biogenic SOA (bSOA) mass in the particulate phase increases by 14% for 5% yield on by 34% and 44% the 10 and 15% yields, respectively. The bSOA concentration increase compared to the base case (no extremely low volatility organics) reaches a maximum of 20%, 45% and 75% for the three cases, respectively (Fig. 3.16b). For cases 10% and 15% yields, this increase of mass of bSOA is significant and results in unrealistically high OA concentrations.
3.16 a) The mass concentration and b) the percentage bSOA increase due to extremely low volatility organic vapor condensation at Hyytiala for different yields. The red line corresponds to a 5% yield, the blue line 10% and the green line 15%.

3.4 Contribution of chemical aging of biogenic SOA

As discussed in section 3.3 if a fraction of mass of the organics is “moved” to the low-volatility bins, the predicted growth of the new particles is similar to the observed. Here we assume that this mass is produced from a chemical aging reaction in which semi-volatile organics react in the gas phase with the hydroxyl radical producing extremely low volatility organics. In the model, the oxidation of biogenic VOCs produces semi-volatile organics with saturation concentrations of 1, 10, 10^2 and 10^3 μg m⁻³ (base case). Our assumption here is that these organics react and produce extremely low volatility organics with saturation concentration of 10⁻³ μg m⁻³ (Pierce et al., 2011). This choice of chemical aging reaction is not expected to cause a large increase of the mass of biogenic SOA.

We tested the effect of the potential aging reaction of biogenic VOCs of the four effective saturation concentrations in the Volatility Basic Set. The aging reactions of organics with saturation concentration of 10, 10^2 and 10^3 μg m⁻³ produce enough additional organic mass in particulate phase to make the results unrealistic. These organic components exist mainly in the gas phase and a reaction with the hydroxyl radical will produce significant amounts of mass in the particulate phase, changing dramatically the total mass of particles. The simulations at Hyytiala (with σ=0.025 N m⁻¹) for a typical day with nucleation and using a chemical aging
reaction in which the organics with $C^* = 1 \mu g m^{-3}$ react with hydroxyl radical producing organics with $C^* = 10^{-3} \mu g m^{-3}$ helps the growth of the particles and also does not change significantly the SOA mass. For this reaction we use a reaction constant of $k = 10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is the same as the one used in Murphy et al. (2012) for the aging of aSOA.

**FIGURE 3.17** Comparison of (a) measured and (b) predicted (with biogenic aging and $\sigma=0.025$ N m$^{-1}$) dry size distribution as a function of time at Hyytiala for a typical nucleation event day.

**FIGURE 3.18:** a) Mass fraction of fresh particles and b) Predicted mass fraction of SOA for the different volatility bins as a function of time at Hyytiala. Simulation includes biogenic aging reaction and $\sigma=0.025$ N m$^{-1}$.
The aging reaction of the $C^* = 1 \, \mu g \, m^{-3}$ component of bSOA results in a growth rate of 2.2 nm h$^{-1}$ and a final diameter of 23 nm. These are similar to the observed values of growth rate of 2.1 nm h$^{-1}$ and diameter of 21 nm (Pierce et al., 2011) (Fig 3.17). In the beginning the new particles consist mainly of ammonium sulfate and a small amount of organics (Fig 3.18a). This small fraction of organics is extremely low-volatility organics ($C^* = 10^{-3} \, \mu g \, m^{-3}$) which are produced from the aging reaction of biogenic (Fig 3.18b). During the day, the new particles grow and the mass of organics increases. The low volatility material dominates the growth during the first few hours, while the semi-volatile ($C^* = 1, 10$ and $100 \, \mu g \, m^{-3}$) dominates the growth during the later stages. At 18:00 the new particles consist mostly (90%) of organics 40% low volatility and 60% semi-volatile (Fig 3.18). The semi-volatile SOA contributes to growth when the particles pass the size beyond which the Kelvin effect is not important. The aging reaction affects new particles at the beginning of growth when the particles are very small.

Figure 3.19 shows how the bSOA concentration changes because of the biogenic aging reaction. As expected, the use of chemical aging reaction increases the mass of bSOA in particulate phase, but the increase is less than 15%. As a results these concentration are consistent with the increase SOA yields measured in the laboratory and used by DMAN.

**FIGURE 3.19** a) The mass concentration of bSOA and b) increase of bSOA compared to the non-aging case at Hyytiala as a function of time.

The assumed biogenic aging reaction helps new particles to grow to larger sizes in Finokalia too and predictions are now consistent with field measurements (Fig.3.20). The predicted growth rate is 4.7 nm h$^{-1}$ while the typical measured growth rate is around 5 nm h$^{-1}$. 
FIGURE 3.20 Comparison of (a) measured (Pikridas et al. 2012) and (b) predicted dry size aerosol distribution (with biogenic aging reaction and $\sigma=0.025$ N m$^{-1}$) as a function of time at Finokalia.

FIGURE 3.21: a) Predicted mass fraction of fresh particles and b) predicted mass fraction of SOA for each volatility bin as a function of time at Finokalia. The simulation includes the biogenic aging reaction (converting $C^*=1$ $\mu$g m$^{-3}$ to $C^*=10^{-3}$ $\mu$g m$^{-3}$) and $\sigma=0.025$ N m$^{-1}$.

The revised model can reproduce the observed growth rate and the final size. At the start of the growth, the new particles consist of 85% $(\text{NH}_4)_2\text{SO}_4$ while at the end of the day this drops to 55%. The organic components initially comprise 15% of the nucleated particle mass, and are mostly of low volatility (75% is from the $C^*=10^{-3}$ $\mu$g m$^{-3}$ volatility bin). During the day this
fraction of the organics increases and reaches a maximum value of 45%. At that point this organic component consists of 30% low-volatility and 70% semi-volatile organics. The reaction of biogenic aging converting $C^* = 1 \mu g \ m^{-3}$ to $C^* = 10^{-3} \mu g \ m^{-3}$ in consistent with the existing laboratory yields.
Chapter 4

Conclusions
4.1 Conclusions

The extended model was evaluated in two locations, at Hyytiala (Finland) and Finokalia (Greece). The model shows that the condensation of organics (when neglecting the Kelvin effect) increases the size of all particles. The freshly nucleated particles grow faster and reach larger diameters. The condensation of organics with zero surface energy affects the number concentration of particles increasing $N_{100}$ and $N_3$. Fresh particles at Hyytiala consist mainly of organics with saturation concentrations of 1 and 10 μg m$^{-3}$ increasing significantly the mass of new particles, while at Finokalia the organic components play an important role for the growth. By increasing the surface tension, the growth rate of new particles decreases and these reach smaller final diameters. The mass concentration of nucleation mode decreases but the increase of the surface tension does not change the temporal evolution of the composition of new particles at Finokalia. The number concentration of particles, which can act as CCN ($N_{100}$), increases with an increase of surface tension in Finokalia, while it decreases at Hyytiala. The concentration of $N_3$ decreases by increasing the surface tension, while this decrease of $N_3$ is larger at Hyytiala than at Finokalia. The effect of surface tension on the number concentration depends on the new particles and the pre-existing aerosol in each location.

The condensation of organics with zero surface tension resulted in a predicted growth rate similar to the field measurements, but the zero value of surface tension is unrealistic. Using realistic value of surface tension shows that the semi volatile organics condensation is not enough to grow the new particles to sizes comparable to those observed. Production of very low-volatility components can better explain this growth. We assumed that 5% of organics, which are produced from the oxidation of biogenic VOCs, have extremely low volatility with saturation concentration of $C^* = 10^{-3}$ μg m$^{-3}$. This simulation along with a surface tension of 0.025 N m$^{-1}$ predicted a growth rate much closer to the measurements, without significant increases in particulate mass. The other two cases considered (10% and 15% of organics forming low volatile organic components with saturation concentration of $C^* = 10^{-3}$ μg m$^{-3}$ and surface tension of 0.025 N m$^{-1}$) showed higher growth rates but the increase of the particulate mass was unrealistic. However, these simulations are not consistent with the existing yield measurements of SOA formation in laboratory experiments.
Assuming that biogenic SOA chemically age and produce extremely low volatility organics (i.e. with a saturation concentration of $10^{-3}$ μg m$^{-3}$) results in predicted grow rates close to the measurements and does not change significantly the total mass of the particles. At Hyytiala, the very low volatility organics condense onto particles smaller than 3 nm. After the new particles grow enough and the Kelvin effect is small, the semi volatile organics are the major components controlling the growth of the nucleated particles. At Finokalia, the model successfully predicts the particle size distribution with condensation of organics ($\sigma=0.025$ N m$^{-1}$) and aging of biogenic. The condensation of organics at Finokalia plays a complementary role for the growth of nucleated particles. After the condensation of sulfates, the organics help the particles to grow to larger diameters. The chemical aging of biogenic SOA contributes to the growth of the nucleated particles because of the extra mass added from the aging reactions. A small fraction of this mass goes to fresh particles resulting in the increase of diameter. There have been no laboratory experiments able to confirm or reject the occurrence of the hypothesized reaction. This reaction is chemical reasonable but suitable experiments need to be designed to test our proposed explanation.

4.2 References


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