Atmospheric particle formation in spatially and temporally varying conditions

Johanna Lauros

Division of Atmospheric Sciences
Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

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“...try to take over the world.”
Atmospheric particle formation in spatially and temporally varying conditions

Toini Johanna Christine Lauros
University of Helsinki, 2011

Abstract

Atmospheric particles affect the radiation balance of the Earth and thus the climate. New particle formation from nucleation has been observed in diverse atmospheric conditions but the actual formation path is still unknown. The prevailing conditions can be exploited to evaluate proposed formation mechanisms. This study aims to improve our understanding of new particle formation from the view of atmospheric conditions.

The role of atmospheric conditions on particle formation was studied by atmospheric measurements, theoretical model simulations and simulations based on observations. Two separate column models were further developed for aerosol and chemical simulations. Model simulations allowed us to expand the study from local conditions to varying conditions in the atmospheric boundary layer, while the long-term measurements described especially characteristic mean conditions associated with new particle formation.

The observations show statistically significant difference in meteorological and background aerosol conditions between observed event and non-event days. New particle formation above boreal forest is associated with strong convective activity, low humidity and low condensation sink. The probability of a particle formation event is predicted by an equation formulated for upper boundary layer conditions. The model simulations call into question if kinetic sulphuric acid induced nucleation is the primary particle formation mechanism in the presence of organic vapours. Simultaneously the simulations show that ignoring spatial and temporal variation in new particle formation studies may lead to faulty conclusions. On the other hand, the theoretical simulations indicate that short-scale variations in temperature and humidity unlikely have a significant effect on mean binary water–sulphuric acid nucleation rate.

The study emphasizes the significance of mixing and fluxes in particle formation studies, especially in the atmospheric boundary layer. The further developed models allow extensive aerosol physical and chemical studies in the future.

Keywords: atmospheric aerosols, particle formation, mixing, numerical modelling
List of Publications

The thesis consists of an introductory review followed by five research articles, which are cited according their roman numerals in the introductory part. The articles are reproduced with the kind permission of the journals concerned.


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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Atmospheric aerosol particles affect the radiation balance of the Earth and thus climate. Climate affects human welfare directly through meteorological conditions and indirectly, e.g., through prevalence of flora and diseases. The prediction of climate change is an extensive challenge for humankind. Reliable predictions require that all the processes which are able to shape climate have to be understood in detail – including the role of atmospheric particle formation.

Aerosol particles are able to affect climate directly, as they mostly scatter solar radiation and thereby cool down the atmosphere. On the other hand, especially black carbon and dust absorb solar radiation, which results in diabatic heating and possibly affects general circulation, humidity and cloud cover (Huang et al., 2006; Perlwitz and Miller, 2010). In addition, aerosols may act as cloud condensation nuclei (CCN) and thus influence radiative properties of clouds and the total radiation balance of the Earth.

The lifetime of an atmospheric particle extends only up to a few weeks in the troposphere. Therefore particles affect atmospheric conditions (air quality, climate) mainly near sources, even if anthropogenic and dust particles can be transported between continents (e.g. Heald et al., 2006; Huang et al., 2010). The local particle concentration varies from tens of particles in a cubic centimetre of clean arctic air (e.g. Koponen et al., 2003) up to $10^5$ particles in a very polluted area (e.g. Mönkkönen et al., 2005; Rose et al., 2010). Observed concentrations have achieved even $10^6$ particles per cubic centimetre during new particle formation events at the coast of Ireland (O’Dowd et al., 2002).

Particles can be formed by two different mechanisms. Primary particles (e.g. dust, sea spray, biomass burning emissions) are emitted directly in all size classes with diameters ranging from nanometres to micrometres while secondary particles are formed through gas-to-particle conversion and are ca. 1–2 nm in diameter. The participating vapours in secondary particle formation are still unknown and several formation paths have
been proposed. Depending on the formation mechanisms and the age of atmospheric particles, the size of particles ranges over orders of magnitude.

The local particle concentration depends on mixing of air – weak mixing can be sensed as poor air quality when high anthropogenic emissions are not mixed from the surface to higher altitudes, e.g., on stable winter days in the Nordic countries. Kukkonen et al. (2005) found that PM10 episodes in European cities were best predicted by temporal evolution of temperature inversion, atmospheric stability and wind speed. Secondary particle formation seems to be connected to solar radiation (e.g., Birmili and Wiedensohler, 2000; Boy and Kulmala, 2002) which indicates the essential role of photochemical reactions in particle formation. However, similar connection has been observed between the onset of secondary particle formation and turbulence (Nilsson et al., 2001b).

Dilution, decrease of background aerosol concentration, due to mixing and dispersion of chemical compounds and aerosols to higher altitudes may create favourable conditions for new particle formation and growth. Hence, spatially and temporally varying meteorological conditions and mixing of vapours and particles have to be considered when the formation mechanisms of secondary particles are traced.

1.2 OBSERVATIONS ON PARTICLE FORMATION

Secondary particle formation can be detected as formation of a new distinct nucleation mode in a particle size distribution. If new particle formation and growth occur over a wide area, particle growth over several hours can be detected (Fig. 1.1). Particle formation has been observed in clean and cold conditions, like the arctic boundary layer and the upper troposphere, likewise in warm and polluted conditions in metropolises (Kulmala et al., 2004c).

The frequency of new particle formation events varies greatly between sites and seasons. Paris et al. (2009) analysed monthly vertical particle profiles from 5 years and reported the highest ultrafine particle concentrations in the mid- and upper troposphere over Novosibirsk, Siberia, in summer. At the surface, in the boreal forest, the maximum particle formation frequency and new particle concentration have been observed in spring and autumn (Dal Maso et al., 2005; Paris et al., 2009). The spring maximum has been explained by increased solar radiation, mixing and chemical activity, especially increased emission of organic compounds. Similarly, Yoon et al. (2006) observed spring and autumn maxima in particle formation frequency at Mace Head and explained this with emissions from marine biota. Especially an essential role of iodine in Mace Head particle formation events has been proposed. On the other hand, in Hohenpeissenberg near the Alps, the maximum formation frequency has been observed in winter and spring, which suggests that new particle formation at this site is controlled by inorganic chemistry (Birmili et al., 2003).
1.2. OBSERVATIONS ON PARTICLE FORMATION

Often new particle formation is coupled to micro- and mesoscale activity in the atmosphere. Paris et al. (2009) concluded that lifting of boundary layer air may enhance ultrafine particle concentration in the mid- and upper troposphere. The authors suggested that particles were formed in situ, because the lifetime of freshly formed particles is short and the observed concentration of 3–70 nm particles was relatively high in comparison to 70–200 nm particle concentration. Already earlier studies (e.g. Clarke et al., 1998; Twohy et al., 2002) connected particle formation to outflow of clouds in the free troposphere and concluded that convection leads to high relative humidity, enhanced concentrations of precursor gases and decreased surface area of particles due to rain-out (in-cloud scavenging of particles) in the mid-troposphere.

Studies suggest that mixing of air with different thermodynamical properties favour new particle formation. In a recent study Peter et al. (2010) observed a connection between particle formation and mesoscale circulation in cold fronts. The upper tropospheric studies have indicated that the mixing of stratospheric and tropospheric air masses, e.g. in connection with a tropopause fold, may lead to new particle formation (Khosrawi and Konopka, 2003; Young et al., 2007). On the other hand, Nilsson et al. (2001b) highlighted the connection between particle formation and boundary layer growth at a boreal forest measurement site. The authors explained that entrainment and turbulent diffusion results in a dilution of background aerosols and a decreasing sink in the boundary layer, whichfavours new particle formation. In addition, the observations showed that mixing was stronger on event days than on non-event days. Nilsson et al. (2001b) suggested a possibility of particle formation in the residual layer above the growing atmospheric boundary layer. Later observations have supported presumed particle formation in the residual layer and the transport of freshly formed
particles to the surface (Stratmann et al., 2003; Siebert et al., 2007; Laakso et al., 2007; Wehner et al., 2010).

Even if observations in certain conditions can be explained by a proposed nucleation mechanism (e.g. Clarke et al., 1999; Jung et al., 2010), no single particle formation mechanism has been able to explain observations globally. New particle formation in divergent conditions leaves open the possibility that there are several new particle formation mechanisms.

1.3 OBJECTIVES OF THE STUDY

Atmospheric conditions vary already in a short distance and time scale, which raises the question if particle formation can be considered in averaged conditions. In general circulation and weather prediction models micro- and mesoscale phenomena are ignored in aerosol calculations as the processes occur in sub-resolution scale. Thus, particle dynamic simulations are based on temporal and spatial means.

In this thesis, particle formation, especially that occurring above the surface layer, has been studied. However, regular measurements are mostly limited to the lowest part of the atmospheric boundary layer and vertical profiles are temporally and spatially coarse or lacking totally, e.g. vertical profiles of precursor vapours. In simulations, we have utilised column models, which do not include a representation for advection or large eddies. These limitations have lead to simplifications in implementation and the complicated interpretation of the results.

This thesis concentrates on the study of how microscale meteorology contributes to secondary particle formation. The main objectives of the study are to

- develop a parametrisation to describe the effect of sub-resolution scale variation on binary water–sulphuric acid nucleation, and to study the significance of temperature and concentration variations in nucleation (PAPER I)
- further develop models which are convenient for gas and particle flux studies, and to evaluate particle formation mechanisms, kinetic and organic-induced nucleation, against measurements in spatially and temporally varying atmospheric conditions (PAPER III and IV)
- study significance of mean micro- and synoptic scale conditions in particle formation (PAPER II and V).
Chapter 2

Atmospheric Conditions

Atmospheric conditions can be considered at various spatial and temporal scales from local micrometeorology (length scale up to 1 km) to synoptic scale conditions (length scale over 1000 km). Air mass analyses and probability studies have highlighted the significance of atmospheric mean conditions in aerosol formation (e.g. Nilsson et al., 2001a; Buzorius et al., 2003; Hyvonen et al., 2005; Sogacheva et al., 2005). Mean properties of an air mass depend, e.g. on characteristics of underlying surface as the air mass exchange heat, moisture and other vapours with the surface. However, the adaption is slow and therefore the properties are affected by air mass history (PAPER V).

While the synoptic situation defines the mean conditions, physical and chemical circumstances vary on a much shorter scale in the atmosphere. Local variation may be generated by turbulent mixing in unstable parts of the atmosphere or by atmospheric waves in stable parts of the atmosphere. Especially, the significance of microscale variation has been considered in PAPER I–IV focusing on the new particle formation in the atmospheric boundary layer.

2.1 Atmospheric Boundary Layer

Several aerosol studies have concentrated on particle formation in the atmospheric boundary layer (ABL), where the atmosphere is directly affected by the Earth’s surface. The height of ABL is controlled by turbulence, which is produced by a wind velocity gradient (kinetic turbulence) or a temperature gradient (thermal turbulence, buoyancy). If the evolution of the ABL is predominantly driven by thermal turbulence, i.e. shortwave radiation heating at the surface and resulting turbulent heat flux to higher altitudes, the layer is called the convective boundary layer (CBL).

When the ABL begins to grow, boundary layer air is mixed in the entrainment zone with air from the neutrally stratified residual layer (Fig. 2.1). In the near-adiabatic residual layer the particle concentration depends mainly on the concentration of the
Figure 2.1: The CBL is capped by a temperature inversion which level can been defined, e.g. as the maximum of the distance corrected SODAR echo (red colour) or from radiosonde soundings (blue square).

previous day. If the air in the free troposphere is cleaner than in the ABL, mixing may lead to a dilution of background aerosol concentration and thus favouring conditions for new particle formation. In addition, the temperature lapse with height lowers saturation vapour pressure and assists new particle formation and growth – the saturation ratio of an organic vapour in an ascending air parcel is considered in PAPER II.

After sunset, radiative cooling of the surface causes the disappearance of convection, and possibly the lowest part of the ABL stabilises. Simultaneously, vapour emissions from vegetation decrease and chemical reactions slow down as a result of reduced radiation and lower temperature. However, atmospheric particles continue growing due to condensing of vapours and coagulation of particles.

2.2 MIXING PARAMETRISATIONS

Meteorological, chemical and aerosol measurements are mostly conducted in the lowest part of the ABL and do not describe well the entire ABL. Model simulations allow us to expand the study from local surface conditions to the entire ABL. However, the spatial and temporal resolution of atmospheric models is limited and even large eddies are not described explicitly in prognostic weather models. The mixing parametrisations aim to describe the effect of sub-time step scale fluxes of momentum, temperature
2.2. MIXING PARAMETRISATIONS

and scalars (aerosols and vapours).

In this study we have utilised two column models, SOSA and MALTE, which simulate temporal and spatial evolution of vapours and aerosol concentration in the ABL. In a column model horizontal advection is ignored and the prognostic equation for a scalar \( s \) simplifies to the form

\[
\frac{\partial s}{\partial t} = - \frac{\partial (s'w')}{\partial z} + S_s. \tag{2.1}
\]

Here \( S_s \) represents source and sink terms of the scalar. \( s' \) and \( w' \) are the instantaneous deviations from the mean values for scalar and vertical velocity, respectively. The overline denotes a mean value. A common way to parametrise the kinematic flux \( s'w' \) is based on the diffusion coefficient \( K_z \) and a local gradient of variable, known as K-theory:

\[
\overline{s'w'} = -K_z \frac{\partial s}{\partial z}. \tag{2.2}
\]

For the first order parametrisations, \( K_z \) depends on a predefined turbulence scale (mixing length) and mean values of wind speed. Alternative first-order representations for \( K_z \) are included also in the original version of MALTE (Boy et al., 2006). However, the first order parametrisations have not described mixing successfully in all conditions and therefore a more sophisticated one-and-half-order turbulence parametrisation (Sogachev et al., 2002) has been implemented in MALTE (PAPER IV).

Sogachev et al. (2002) applied turbulent kinetic energy \( e \) to formulate the diffusion coefficient \( K_z(e) \). The solution is a one-and-half-order parametrisation, meaning that the turbulent kinetic energy and the specific dissipation \( \omega \) have a prognostic equation (e.g. Sogachev, 2009). The turbulent kinetic energy depends on vertical transport of existing turbulent kinetic energy, production of mechanical and thermal turbulence, dissipation and sources and sinks due to interaction with canopy elements \( S_E \) (Sogachev 2009; PAPER III):

\[
\frac{\partial e}{\partial t} = \frac{\partial}{\partial z} \left( \frac{K_z}{\sigma_e} \frac{\partial e}{\partial z} \right) + K_z \left[ \left( \frac{\partial u}{\partial z} \right)^2 + \left( \frac{\partial v}{\partial z} \right)^2 \right] - K_z \left[ \frac{g}{T} \left( \frac{\partial T}{\partial z} + \gamma_a \right) - \frac{0.618}{\rho} \frac{\partial q}{\partial z} \right] + \omega e + S_E. \tag{2.3}
\]

Here \( \sigma_e \) is the Schmidt number for turbulent kinetic energy and \( \sigma_H \) is the Prandtl number, \( u \) and \( v \) are the horizontal wind components, \( T \) is temperature and \( q \) specific humidity, \( g \) is the gravitational acceleration, \( \gamma_a \) is the dry adiabatic lapse rate and \( \rho \) is the density of air. The evolution of specific dissipation \( \omega \) is predicted in similar manner as \( e \) with proper terms for its sources, sinks and transport. PAPER III shows that the implemented turbulence scheme succeeds to reproduce observed profiles of meteorological variables in the surface layer where small eddies dominate.
Parametrisations could be developed to higher and higher order terms. For example, Hellmuth (2006b) successfully utilised a second order parametrisation in a boundary layer aerosol study. In this model version second order terms, variances and covariances, have prognostic equations while the third order terms are parametrised.

Even if higher order terms are predicted, the conventional form of Eq. (2.2) describes always mixing between two adjacent layers, and fluxes depend on local scalar gradients. Instead, large eddies extend even through the whole CBL carrying most of the turbulent kinetic energy (Stull, 1993), and thus fluxes at the top of the ABL do not depend only on local gradient, but also on temperature gradient at the surface. Noh et al. (2003) concluded from large eddy simulations, that local wind shear production was not able to explain turbulent kinetic energy in the inversion layer. In addition, Eq. (2.2) generates always a flux from a higher to a lower value, as $K_z$ is positive. This is not a valid assumption at the top of the convective boundary layer due to buoyancy-born large eddies (see e.g. Siebesma et al., 2007).

Observations (e.g. Stratmann et al., 2003) support the view that atmospheric particles are formed in or above the upper part of ABL. Therefore mixing at the top of the ABL and large eddies should be reproduced reliably in aerosol studies. In the present work (PAPER III–IV), the representation of local mixing and especially the influence of canopy were prioritised over a specific large eddy representation. In the future, the large-eddy representation should be considered. One solution is the asymmetric or two-stream column model, which presents the descending and ascending branch of large eddy circulation separately. These models have been exploited successfully in vapour flux studies (Han and Byun, 2005; Pleim, 2007; Vautard et al., 2007). On the other hand, non-local mixing has been described by a separate gradient adjustment term $\gamma_C$ in prognostic equations. A common feature of the implemented representations (e.g. Abdella and McFarlane, 1997; Noh et al., 2003) is that $K$ and $\gamma_C$ depend on surface flux of parametrised variable, and therefore the representations cannot be adapted to vapour and aerosol flux parametrisations without a critical consideration. The added gradient adjustment term may cause a result that is opposite to the intended effect, e.g. if new particle formation occurs solely above the surface layer in a convective situation. When gradient adjustment should result in larger fluxes than the conventional form of Eq. (2.2), the resulting fluxes may be smaller.
NEW PARTICLE FORMATION AND DEPOSITION

According to present conceptions, new particle formation begins with nucleation of clusters of few nanometres in diameter followed by condensational growth. However, observations on freshly formed neutral clusters, which are smaller than 3 nm in diameter, did not exist until recently when Sipilä et al. (2010) were able to measure particles down to 1.3 nm in diameter. As the composition of freshly formed neutral clusters cannot be directly defined, the actual particle formation mechanism is still unknown.

3.1 VAPOURS AND EMISSIONS

Sulphuric acid H$_2$SO$_4$ and reaction products of organics are the most essential vapours that participate in nucleation. Sulphuric acid has a low saturation vapour pressure and therefore it is a potential participant in atmospheric nucleation. Observed H$_2$SO$_4$ concentrations have been on average higher on event than on non-event days in Hohenpeissenberg and at SMEAR II (Birmili et al., 2003; Petäjä et al., 2009). Sulphuric acid is formed through oxidation of sulphur dioxide SO$_2$ and has a clear diurnal cycle and a daytime maximum. Natural sources for SO$_2$ are, e.g. oceans (algae), volcanoes, forest fires and biological decay but a large portion of emissions is still anthropogenic despite reduction efforts (Vestreng et al., 2007; Manktelow et al., 2007). The most important anthropogenic SO$_2$ source is combustion of coal and petroleum (Smith et al., 2010). Sources of volatile organic compounds (VOCs) are mostly biogenic, e.g. emissions from boreal and tropical forests (Guenther et al., 2006; Goldstein and Galbally, 2007). Even if emitted organic vapours are volatile; it is the reaction products of VOCs that are more apt to condense participate in particle formation.

Most important oxidising compounds in the atmosphere are hydroxyl radical OH, ozone O$_3$ and nitrate radical NO$_3$. The oxidising compound determines how the concentration of organic reaction products behaves temporally (Fig. 3.1). As OH is formed through photochemical reactions, its concentration has a clear diurnal cycle. Tropo-
3.2 NUCLEATION AND PARTICLE GROWTH

Due to kinetic energy, vapour molecules collide with each other and form molecular clusters. In favourable conditions the size of formed clusters exceeds the critical radius, i.e. clusters become thermodynamically stable, and continue growing more likely than break apart. This gas-liquid phase change is called nucleation. If the thermodynamically stable clusters (TSC) continue growing to a detectable size, a new particle formation event can be observed. As new particle formation has been observed widely in divergent conditions, several nucleation mechanisms have been proposed, e.g. binary, ternary, ion-induced and organic-induced nucleation. Common for suggested formation mechanisms is that sulphuric acid is involved in the nucleation and growth processes.

The observed formation rate of 3 nm particles is typically 0.01–10 cm$^{-3}$s$^{-1}$ but ex-
ceeds this in highly polluted areas and coastal zones (Kulmala et al., 2004c). The most studied binary H$_2$O–H$_2$SO$_4$ nucleation mechanism has succeeded in reproducing observed new particle formation rates in the tropical free troposphere in the presence of clouds (Clarke et al., 1999), but most of cases the theory predicts nucleation rates that are too low. Discrepancies between observations and theoretical nucleation rates have been explained by varying conditions (Easter and Peters 1994; Paper I) or mixing of dissimilar air masses (Khosrawi and Konopka, 2003).

As the binary theory has failed to reproduce observations, several studies have focused attention on ternary H$_2$O–H$_2$SO$_4$–NH$_3$ nucleation (e.g. Napari et al., 2002). Ammonia stabilises H$_2$O–H$_2$SO$_4$ clusters providing a higher nucleation rate than binary nucleation. In spite of promising results in polluted areas (Jung et al., 2010), the ternary nucleation theory has not generally succeeded in reproducing observed particle formation rates. Recent studies (e.g. Kurtén et al., 2008; Loukonen et al., 2010) have shown that amines are able to enhance the addition of sulphuric acid to a cluster more efficiently than ammonia. Therefore the role of amines in nucleation will be an interesting topic in the future.

Empirical studies indicate that observed particle formation rate correlates with sulphuric acid concentration linearly or quadratically, while the binary nucleation theory predicts a higher order dependence. As an answer to this discrepancy, Kulmala et al. (2006) exploited collision type nucleation theory (e.g. McMurry, 1980; Weber et al., 1996) and the kinetic nucleation rate:

$$J = K [\text{H}_2\text{SO}_4]^2$$

Here the pre-factor $K$ describes the probability that a collision of two sulphuric acid molecules leads to new particle formation and the upper limit for $K$ is the kinetic molecular collision rate. The magnitude of $K$ has been defined to be between $10^{-14}$ and $10^{-10}$ cm$^{-3}$ s$^{-1}$ in southern Finland and in Heidelberg varying over orders of magnitude (e.g. Sihto et al., 2006; Riipinen et al., 2007). Similarly, the pre-factor has been defined in cases which show a linear dependence of nucleation rate on H$_2$SO$_4$ concentration indicating activation of existing clusters by H$_2$SO$_4$. In a recent study Paasonen et al. (2009) suggested that the pre-factors depend on the concentration of organic vapours.

Freshly formed nano-size particles have to grow fast enough to avoid coagulation to larger particles but in most cases H$_2$SO$_4$ cannot be responsible for observed condensational growth (Boy et al., 2003). Kulmala et al. (2004b) observed that the growth rate depends on particle size and concluded that this can result from different nucleating and condensing vapours. Assuming sulphuric acid-induced nucleation, Kulmala et al. (2004a) introduced the nano-Köhler theory which describes activation of 1–3 nm nucleated clusters by organic vapours. The theory complies with the hypothesis that nucleation does not limit new particle formation but TSC are activated and grow to
observable 3 nm size only under favourable conditions (Kulmala et al., 2000).

Recent studies have proposed that low-volatility organic vapours could contribute to nucleation (Paasonen et al., 2009; Metzger et al., 2010; Vuollekoski et al., 2010). In this thesis (PAPER IV), we found that organic-induced nucleation seems more compatible with observations than kinetic nucleation (represented by Eq. 3.1), despite the fact that the exact participating organic vapours in nucleation and growth are still unknown. Organic-induced nucleation was able to reproduce the observations that new particle formation takes place in the ABL (Laakso et al., 2007), while the kinetic nucleation theory generates a maximum of particle concentration above the ABL due to a low condensation sink.

Two alternative organic-induced formation paths are presented in PAPER IV. If the atmospheric nucleation is organic-induced, the observations of new particle formation events almost exclusively during the daytime suggests that the nucleating organic compounds form in an oxidation reaction with OH. This is because the simulated formation rate has a clear diurnal cycle. If reaction products from organics oxidised by NO$_3$ or O$_3$ are participating in nucleation, the observed daytime events have to result from diurnal variation of H$_2$SO$_4$, restrictive nano-Köhler growth or mixing. However, products of organics oxidised by O$_3$ as a nucleating compound lead to continuous particle formation in the study presented in PAPER IV. Neither diurnal cycle of H$_2$SO$_4$ nor nano-Köhler growth is able to control particle formation if nucleation occurred constantly and in situ in the ABL.

### 3.3 Deposition

The concentration of smallest particles decreases due to condensational growth to larger sizes and coagulation to larger particles but particles are removed entirely from the atmosphere through wet and dry deposition. Wet deposition, rain-out (removal of CCN), wash-out in clouds and sweep-out below clouds, are more effective than dry deposition but simulation of wet deposition requires a representation of cloud formation and precipitation, which are not included in the column models used in this work up today. Besides, new particle formation is observed only in dry weather conditions.

The significance of dry deposition in the boreal forest is studied in PAPER IV. Particles may be removed due to Brownian motion, interception, impaction and gravitational settling. Brownian diffusion to surfaces results from random movement of particles and the process depends primarily on the size of a particle and temperature. Impaction of particles results from inertia: the particle hits an obstacle as it is not able to follow turning streamlines. Even if the particle follows a flow streamline around an obstacle, it may arrive too close to the obstacle causing interception. Brownian diffusion is
the most important dry deposition mechanism for nucleation (\(<\ 30\ \text{nm in diameter})\) and Aitken (20–100 nm) mode particles but the significance of interception increases if the particle size increases (Fig. 3.2) or the wind strengthens (Petroff et al., 2008). For accumulation mode particles (90–1000 nm) impaction exceeds Brownian diffusion already in moderate winds. Gravitational settling has been ignored in the present model version in PAPER IV as it removes primarily particles that are several micrometres in diameter, while the modelled particle distribution is limited below one micrometre.

The improved description of deposition and simulations indicate that dry deposition could be ignored in short-term case studies (PAPER IV). However, deposition plays potentially a more essential role in long-term studies.
CHAPTER 4

OBSERVATIONS AND SIMULATIONS

In this thesis, atmospheric new particle formation was studied by analysing field observations and by performing model simulations. Even if measurements represent only local conditions at a certain time, we can study, e.g., the connection between mean micrometeorological circumstances and new particle formation by extending the measurements over a wider area or a longer time period. However, sometimes extensive measurements are not possible and model simulations are more convenient. To develop efficient models, the importance of physical and chemical processes should be known.

4.1 OBSERVATIONS USED IN THE THESIS

The studies presented in PAPER II–IV utilise primarily observations carried out at the SMEAR II (Station for Measuring Forest Ecosystem-Atmosphere Relations) field research station in southern Finland. The observations have been exploited directly and as input for models. The station area is dominated by coniferous forest. The terrain is rolling and the measurement station is located at the upper part of a hill sloping towards a lake. Kulmala et al. (2001) give a review of measurement systems at the station.

The mast measurements of meteorological variables reach 74 m height. Thus, the measurements cover obviously only the lowest part of the CBL which may grow to a few kilometres high. For this reason most of the daytime measurements at the SMEAR II station are carried out in the surface layer, which covers approximately the lowest 10% of the ABL. The surface layer, however, is the most important source for turbulence, humidity and organic vapours and therefore it is essential also in aerosol formation studies.

In addition to the mast measurements, the mean wind components and standard deviations were measured up to 500 m by SODAR (SOnic Detection And Ranging) and thereby strength of mixing could be studied. The strength of the SODAR echo tells the height of ABL as the capping inversion is seen as a maximum in echo strength – this feature is utilised in PAPER II and IV as an input parameter and to evaluate
4.2 SUB-GRID SCALE NUCLEATION SIMULATIONS

The present day global climate models have a resolution of few degrees or few hundreds of kilometres and the corresponding time step is several minutes. The simulated temperature distribution over southern Finland (Fig. 4.1) shows that significant sub-resolution scale variation of temperature (and vapour concentrations) is potentially ignored in the global models – temperature varies several degrees in a $200 \times 200$ km grid square.

The binary water-sulphuric acid nucleation rate depends non-linearly on temperature and vapour concentrations: a decrease in temperature increases the nucleation rate...
more than an equal but opposite change decreases the rate. Easter and Peters (1994) carried out random simulations and concluded that the nucleation rate in mean conditions may differ from the real mean nucleation rate substantially. The ratio between the real mean nucleation rate $I(T, q, c)$ and the nucleation rate in mean conditions $I(\bar{T}, \bar{q}, \bar{c})$ has been studied with similar theoretical simulations (PAPER I). In simulations, we assume that the variables are normally distributed (see Fig. 4.1b). As a result of the simulations, terms of a correction factor $f$ has been defined:

$$I(T, q, c) = f \cdot I(\bar{T}, \bar{q}, \bar{c})$$

(4.1)

The correction factor has been formulated as a function of mean values, standard deviations and correlation between temperature and specific humidity as the second order turbulence parametrisations are commonly used in large scale models. Even if the main purpose of the turbulence parametrisation is to describe fluxes, the parametrisations produce also variances of variables, which can be exploited by the correction factor.

The carried simulations show that the $I(T, q, c)$ may be even orders of magnitude higher than $I(\bar{T}, \bar{q}, \bar{c})$, as Easter and Peters (1994) already concluded in their earlier study. In practical terms this means that under some conditions onset of nucleation may happen with a half of sulphuric acid concentration that is required in the mean conditions. However, in most cases the difference between the observed and the required sulphuric acid concentration is orders of magnitude. In addition, the correction factor increases as temperature increases and vapour concentrations (water, sulphuric acid) decrease which, on the other hand, decreases the actual nucleation rate. Due to the temperature

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**Figure 4.1:** a) Surface temperature simulated with a resolution of 2.4 km in southern Finland on 14 April 2010 by WRF (Weather Research & Forecasting Model, Skamarock et al. (2005)).

b) Temperature distribution of the 200 × 200 km area, which is outlined in a) ($\bar{T}=287$ K, $\sigma_T = 0.43$ K).
dependence, the correction factor is the largest in the lower atmosphere where other nu-
cleation mechanisms potentially dominate over binary H$_2$O-H$_2$SO$_4$ nucleation. Even
if the mean nucleation rate can increase by orders of magnitude due to variation, the
rate may still remain insignificant.

4.3 BOUNDARY LAYER SIMULATIONS

Developing convenient column models for chemistry and aerosol studies in the ABL
was one of the main objectives in PAPER III and IV. The developed models SOSA
(model to Simulate the concentration of Organic vapours and Sulphuric Acid) and
MALTE (Model to predict new Aerosol formation in the Lower Troposphere) have
been built on similar schemes for meteorology (Sogachev et al., 2002) and chemistry.
MALTE includes also a representation of aerosol physics: nucleation mechanisms, ac-
tivation of nano-size clusters, condensation and coagulation (Korhonen et al. 2004;
Boy et al. 2006; PAPER IV). MALTE was further developed in this study. The new
model version enables more realistic studies than the original version (Boy et al., 2006)
as now the interaction between vegetation and the atmosphere, the surface layer char-
acteristics affecting mixing, radiation and the sources of organic vapours are described
with high vertical and temporal resolution. In addition, in comparison to earlier chemi-
cal and aerosol physical studies (e.g. Vautard et al., 2007; Hellmuth, 2006a), the chem-
istry scheme is extensive, covering VOC emissions and hundreds of reactions in SOSA
and over one hundred reactions in MALTE.

Diabatic heating at the surface produces circulation, especially large eddies, which are
difficult to describe in a column model. This leads unavoidably to compromises. In
PAPER III, the realistic mixing and vertical wind profile have been prioritized, e.g.
over a faithful reproduction of the vertical distribution of local vegetation. The lack
of cloudiness observations can be noticed in the results, as the model does not always
succeed in reproducing observed long wave radiation (PAPER III). While the meteorol-
ogy scheme is satisfactory in near neutral conditions in the surface layer (PAPER III),
the model seems to underestimate mixing at higher altitudes in the tested spring case
(PAPER IV).

PAPER III shows that the simulated profiles of reaction products of organic vapours
are consistent with observations. The result is strengthened in PAPER IV where parti-
cle formation processes have been included in the model. Organic-induced nucleation
leads to observed particle profile while conventional kinetic nucleation fails to repro-
duce the observations. At the same time, PAPER IV shows how box model simulations
may lead to wrong conclusions: even if kinetic H$_2$SO$_4$-induced nucleation fails to
reproduce the observed particle profile, the theory simultaneously succeeds in repro-
ducing the observed local event at the surface.
This thesis consists of five papers concentrating on particle formation simulations in varying atmospheric conditions.

**PAPER I** focuses on the effect of atmospheric variability on binary water–sulphuric acid nucleation. A parametrisation, which describes the effect of sub-grid scale variation on nucleation, has been formulated. The presented theoretical simulations verify earlier results that the variation of temperature and vapour concentrations may increase the mean nucleation rate by orders of magnitude but show that the significant effect is unlikely.

**PAPER II** presents results based on observations in the ABL. The probability of new particle formation is described as a function of characteristic conditions in the upper ABL. The comparisons between event and non-event days show that atmospheric mixing is stronger and saturation ratio of organic vapours in an ascending air flow is potentially higher on event than on non-event days.

**PAPER III** focuses on simulating reliable profiles of various compounds and parameters in the ABL above the boreal forest. For this purpose a chemical column model has been developed and the model has been evaluated against meteorological observations in the surface layer. The simulated organic vapours have a similar vertical concentration profile as the observed freshly formed particles while the simulated sulphuric acid profile is not consistent with the observed particle number concentration profile.

**PAPER IV** continues work which has been started in **PAPER III**. Now a scheme for aerosol physics has been utilised to produce vertical aerosol number concentration profiles. Organic nucleation following growth by organic vapours and sulphuric acid succeeds in reproducing the observed particle profile while kinetic sulphuric acid-induced nucleation fails. Consideration on particle fluxes and deposition indicates that deposition does not significantly affect short-term particle flux.

**PAPER V** focuses on significance of synoptic scale conditions utilising air mass analysis. The observed new particle formation was most frequent and intense at Tumbarumba field station in Australia, when relatively dry air from the Southern Ocean
was passing over the research station. Statistically significant dependence of particle formation events on air flow direction was observed.

**Author’s Contribution**

The author of thesis did the simulations and analyses presented in PAPER I. Conclusions were drawn together with the co-authors. The author wrote a major part of PAPER I. Similarly, the author did the simulations and analyses presented in PAPER II, wrote the mixed layer slab-model, further developed the analysis of SODAR data and wrote a major part of PAPER II. The author contributed in developing the model for PAPER III and wrote a minor part of the publication. The initial idea for PAPER IV was given by the author of the thesis and the co-authors. The author did the simulations and analyses but conclusions were drawn together with the co-authors. The author merged together two atmospheric models and added a scheme for deposition into the model, which was utilised in the study. The author wrote a major part of PAPER IV. The author contributed in the analysis of results (significance of latent heat flux) which are presented in PAPER V.
CONCLUSIONS AND DISCUSSION

The study deepens our understanding of particle formation in varying atmospheric conditions. The model simulations concentrate on microscale processes while the long-term observations describe as well synoptic scale conditions.

The probability of new particle formation events is presented as a function of mean microscale variables at the top of the ABL. The most essential variables are condensation sink and temporal change of temperature. The values of variables in the upper ABL have been derived from surface measurements which can, to a large degree, explain the consistency with earlier studies. The presented calculations are based on several simplifications, e.g. constant concentration of dry particles in an ascending air parcel and a non-existent entrainment zone above the ABL. Lagrange type box model simulations would have allowed the description of particle dynamics in an ascending air parcel. Furthermore, 1D or 3D model simulations would have also given more reliable meteorological profiles.

The observations at Tumbarumba field station highlight the importance of spatially varying conditions in new particle formation. In the studied case latent heat flux far from the measurement station most probably determines the probability of new particle formation. The significance of air mass history in synoptic scale should be noticed when, e.g. results of column model simulations are evaluated and analysed.

The theoretical model study verifies that temporal or spatial variation in temperature and vapour concentrations can increase the mean binary water-sulphuric acid nucleation rate by orders of magnitude. The effect of this variation has been parametrised with a correction factor. Under atmospheric conditions, however, the factor is significant only in limited cases. The factor is largest at high temperature and low humidity while these conditions inhibit binary H$_2$O–H$_2$SO$_4$ nucleation. Even if binary nucleation could reach a significant level locally or momentarily, the variation cannot explain the orders of magnitude difference between observed and theoretical nucleation rates. Therefore, the sub-grid scale variation can be ignored in most of nucleation calculations in large scale models.

The further developed column models SOSA and MALTE succeed to produce reliable
physical and chemical conditions in the ABL. The main result of column model sim-
ulations is that conventional H₂SO₄-induced kinetic nucleation is unlikely the primary 
particle formation mechanism in the ABL in the presence of organic vapours in the 
boreal forest. The results encourage continued studies on organic-induced nucleation.

The column model simulations highlight especially the importance of atmospheric 
mixing and local micrometeorological conditions in aerosol studies – the conclusions 
on possible nucleation mechanisms in the ABL are based on vertical vapour and par-
ticle profiles. Several studies have suggested that new particle formation take place 
near the ABL top. Therefore, the role of large eddies and mixing between the ABL 
and the free troposphere should receive greater attention. A representation for large 
eddies in MALTE should be considered in future. This could enable studies on the 
significance of dilution in new particle formation that are more reliable than with the 
present model version. Measured vertical profiles of precursor vapours and particle 
number distributions would allow evaluation of model results.
REFERENCES


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