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DATA ANALYSIS AND REGIONAL SCALE MODELING OF
ATMOSPHERIC AEROSOLS IN EUROPE

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Academic dissertation

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Data analysis and regional scale modeling of atmospheric aerosols in Europe

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Abstract

Atmospheric aerosols produced from gas-to-particle conversion processes have important impact on the climate and human health. The initial step of this phase change is called nucleation. Nucleated new particles that grow further can directly affect climate by absorbing or scattering the incoming solar radiation, or indirectly by acting as cloud condensation nuclei and thereby changing the lifetime and optical thickness of clouds. This thesis focuses on better understanding the relationship between new-particle formation (NPF) events and different components such as meteorological, atmospheric gas-phase species, and particularly solar radiation and cloudiness.

The solar radiation is an important key to NPF events, which involve photochemistry reactions in the atmosphere. The UV spectrum in particular is important for the formation of radical species such as OH·, which is required to oxidize the atmospheric gas species such as SO₂ and biogenic organic vapors involved in NPF processes. Oxidation of SO₂ leads to production of sulfuric acid, which has been recognized as most important species in NPF events. We showed, however, that the absolute radiation intensity alone cannot explain all NPF event days or the days when no new particles were formed. Clouds attenuate the incoming radiation, thus affecting the production of new particles. We observed that for a quantifiable NPF event to occur, the radiation intensity (I) should be at least about 50% of its maximum possible value (I_{max}). In addition, a clear sky day in spring is a better candidate for NPF event than a cloudy sky day in summer, indicating that relative radiation intensity is a better predictor than radiation intensity itself. We observed that presence of cloud either interrupts or stops the below cloud particle formation. The continuation of particle formation also depends on other components, which favors the NPF events such as lower aerosol surface area (or condensation sink, CS) or high sulfur dioxide concentration. The cloud adjustment scheme for modifying the photolysis rate profiles within PMCAMx-UF, a 3D chemical-transport model, was updated with the TUV (Tropospheric Ultraviolet and Visible) radiative-transfer model. Enhanced new-particle formation is predicted near cloudy regions due to increase in reflected radiation near cloudy regions leading to increased actinic flux, which in turn leads to higher sulfuric acid production.

Another focus of this work is the effort towards more accurate predictions of particle formation rates and their number concentrations. To accurately predict the aerosol number concentrations, the proper NPF mechanism is required. Over the course of the years and remarkable aerosol research advances, different NPF mechanisms have been discovered in which the sulfuric acid vapor is mostly present. Among these, binary mechanism of sulfuric acid-water and ternary sulfuric acid-water-ammonia have been implemented in different aerosol and climate models. To parametrize these mechanisms, different approaches are used. Commonly, Classical Nucleation Theory (CNT) is used in large scale models.

This approach, however, fails to predict the number concentrations. Thus, a dramatically large tuning factor (10^{-5} or 10^{-6}) is usually applied to the model predictions of aerosol number concentrations. In this work, we replaced the CNT-based NPF scheme of the ternary pathway within PMCAMx-UF, a 3D chemical-transport model, with particle formation rates simulated by Atmospheric Cluster Dynamics Code (ACDC), which is based on first-principles calculations. It is shown that the model using the ACDC-based formation rates simulates the number concentrations of particles larger than 4 nm within one order of magnitude of observations without tuning the predictions. This is very promising given the fact that the CNT-based NPF scheme gives reasonable prediction only after applying dramatic tuning factor. Last part of the thesis focuses on estimating the formation rates of the 3 nm particles generated during NPF events at the SMEAR IV station in Kuopio (Finland), where the aerosol measurements extend only down to 7 nm particles. To do this, an analytical formula based on aerosol dynamics was used, with which one can extrapolate the formation rates of larger particles to obtain the formation rates of smaller particles and vice versa. The method was first evaluated on NPF events in Hyytiälä where the aerosol measurements are available for the particle sizes down to 3 nm. The estimated values are found to be in good agreement with the observed ones when comparing the daily mean formation rates, but the detailed time evolution is often poor. The failure to predict the time evolution of particle formation is caused by the unsatisfactory growth rate estimates which required to calculate the time lag between the formation of 3 nm and 7 nm particles. This points to the challenges in predicting atmospheric nucleation rates for locations where the particle growth and loss rates are size and time-dependent.

Keywords: atmospheric new-particle formation, solar radiation, cloudiness, nucleation, TUV, PMCAMx-UF, Atmospheric Cluster Dynamics Code, particle formation rates, particle growth rate

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List of publications

This thesis consists of an introductory review, followed by three research articles. In the introductory part, the papers are cited according to their roman numerals.

- I Baranizadeh, E., Arola, A., Hamed, A., Nieminen, T., Mikkonen, S., Virtanen, A., Kulmala, M., Lehtinen, K. & Laaksonen, A.: The effect of cloudiness on new-particle formation: investigation of radiation levels, *Boreal Env. Res.*, 19 (suppl. B): 343–354, 2014. Reproduced with permission.
- II Baranizadeh, E., Murphy, B. N., Julin, J., Falahat, S., Reddington, C. L., Arola, A., Ahlm, L., Mikkonen, S., Fountoukis, C., Patoulias, D., Minikin, A., Hamburger, T., Laaksonen, A., Pandis, S. N., Vehkamäki, H., Lehtinen, K. E. J., and Riipinen, I.: Implementation of state-of-the-art ternary new-particle formation scheme to the regional chemical transport model PMCAMx-UF in Europe, *Geosci. Model Dev.*, 9, 2741-2754, doi:10.5194/gmd-9-2741-2016, 2016. Reproduced under Creative Commons Attribution License.
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1 Introduction

An *aerosol* is defined as a mixture of fine liquid, solid, or mixed-phase particles in a gas. However, the term *aerosol phase* is commonly used to refer to the particulate matter component only. Air, for example, is an aerosol and the particles floating in it are called aerosol particles. The term aerosol can also refer to technological uses such as aerosol spray, paints, medical treatment by inhalation devices etc.

This thesis focuses on (secondary) *atmospheric aerosols*. Aerosols are either directly emitted to the atmosphere (primary aerosols) or formed in the atmosphere (secondary aerosols) from gas-to-particle conversion processes. This phase transition is initiated with nucleation of vapor molecules (Seinfeld and Pandis, 2006). The species (one or more than one) involved in the nucleation process can nucleate either on a pre-existing foreign surface (*heterogeneous nucleation*) or on the embryos of vapor molecules without another foreign surface present (*homogeneous nucleation*). In this thesis, we are interested in the nucleation of gas molecules (trace substances) and water in their vapor phase (air) to the liquid (droplet) or solid phase. In the initial steps of nucleation, nanometer-size clusters of the new phase are formed. The clusters of new-born particles become stable at a critical size and tend to grow further. The cluster population changes in size and number by competition of two processes: condensation/evaporation and coagulation. Through condensation a vapor compound such as sulfuric acid, ammonia, organic vapors condense on homogeneously or heterogeneously nucleated particles and grow them to larger sizes and form new particles. By coagulation, however, smaller particles can collide with larger size particles and stick together (coalesce) which results in loss of new-born particles and thus less new-particle formation (NPF).

Atmospheric aerosols affect our lives in many important ways, depending on their size and composition. Submicron aerosols can penetrate into the deepest parts of the human lungs and affect our health. Aerosols can both directly (through absorption and scattering of (shortwave) solar radiation) and indirectly, by modifying cloud properties, exert a radiative forcing on climate. The climate effects of aerosol particles can be either warming or cooling. Particles that contain black carbon (soot) absorb radiation and thus have a warming effect, whereas those particles that contain sulfate, nitrate and organic carbon are able to efficiently scatter radiation, and thus have a cooling effect. Most aerosol particles mainly scatter the incoming solar radiation. Thus, on the whole, the direct aerosol effect has a net cooling effect on the global climate (International Panel on Climate Change, IPCC 2013). The indirect effects arise from the fact that cloud drops are formed around aerosol particles - meaning that aerosols act as cloud condensation nuclei (CCN) and hence affect the cloud properties. A higher concentration of aerosols (e.g., more polluted environment than a clean environment) results in that the available water vapor is distributed to a larger number of CCN – thus resulting in a higher number density of cloud droplets thus brighter clouds with a longer lifetime. This is referred to as the indirect effect of aerosols on climate. However, the magnitude of aerosol indirect effects remains the single

largest uncertainty in current estimates of anthropogenic radiative forcing (International Panel on Climate Change, IPCC 2013) and causes large uncertainties in the calculations of future climate change.

Gas-to-particle conversion (nucleation) as the first step of new-particle formation (NPF), or in other words secondary aerosols, is known to be a major source of particles in the atmosphere (Seinfeld and Pandis, 2006). The number concentration of submicron particles is an important quantity when considering the secondary aerosols' role in climate and human health. The mass concentration is usually important when it comes to air quality regulations. In many locations aerosols are regulated by particle mass concentration (e.g. PM_{2.5}; mass concentration of particles with diameter lower than 2.5 µm). However, many studies have shown that ultrafine particles (particle diameter < 100 nm), which in most cases dominate the particle number concentration but only make a minor contribution to the particle mass, may be a major cause of several adverse health effects (e.g., Obersdöster et al., 1996; Peters et al., 1997, Shiraiwa et al., 2012). The aerosol number size distribution is highly relevant also when estimating the aerosol impacts on climate, because the amount of CNN is determined from the aerosol number size distribution. Therefore, to resolve the uncertainty of aerosols indirect effect on climate it is highly necessary to determine the particle size distribution (Ahlm et al., 2013). This is, however, a challenging task due to the lack of measurements in many places. This has led scientists to develop aerosol models and aerosol dynamical theories to better understand and predict the aerosol size distributions also in large scales. This in turn demands a good understanding of aerosol processes as well as aerosol emissions during pre-industrial and present conditions (Carslaw et al., 2013). There still remain many uncertainties concerning these emissions and processes, although substantial progress has been made in understanding aerosol-climate interactions. For example, a global-modelling study by Carslaw et al. (2013) shows that the contribution of uncertainty in natural emissions to indirect radiative forcing is larger than the uncertainty in anthropogenic emissions. The natural emissions in their study included volcanic sulphur dioxide, marine dimethylsulphide, biogenic volatile organic carbon, biomass burning and sea spray. In addition, an experimental study by Kirkby et al. (2016) introduced a NPF mechanism, which may dominate the NPF in pristine environments with low sulfuric acid concentration, since it involves the nucleation of pure organic vapors with ions and oxidized organic vapors as the stabilizing agents. They suggested that nucleation of pure biogenic species could have resulted in more aerosols in the pre-industrial climate than thought before and thus also a lower anthropogenic radiative forcing in the current climate.

More studies are needed to explore the NPF process, to achieve a less uncertain global picture of NPF and, quantify the indirect aerosol effect on past (pre-industrial), current and future climate. Atmospheric models are an important tool in pursuing this goal as they are necessary in predicting the dynamics of the aerosol population. The NPF parametrizations based on Classical Nucleation Theory (CNT) are commonly used in large scale atmospheric models. Due to the unrealistic assumptions (e.g., using bulk properties for nucleated particles), CNT-based NPF schemes have failed to predict the particle formation rates. Thus, CNT-based predictions need to be scaled dramatically. However, recently developed computational models (e.g., the Atmospheric Cluster Dynamics Code; ACDC;

McGrath et al., 2012; Olenius et al., 2013) can now produce the particle formation rates without applying any scaling factor. The ACDC model simulates the kinetics of molecular clusters population and the clusters free energies calculated from first-principles methods such as quantum chemistry.

This thesis investigates the new-particle formation (NPF) phenomenon, its characteristics (e.g., particle formation and growth rates) and the atmospheric parameters, which suppress or cause the NPF events. Solar radiation, for example, is a key driver for photochemistry to produce condensing and nucleating vapors. The methods used are data analysis of in-situ and airborne measurements as well as NPF simulation by a chemical transport model (CTM).

The research questions that were addressed in this thesis are:

1. Can *relative* solar radiation intensity be used as an indicator of the occurrence of NPF events?
2. how does replacing the radiation scheme within PMCAMx-UF with radiative-transfer module *TUV (Tropospheric Ultraviolet and Visible)* affect the predicted particle formation?
3. Are the most recent first-principle-based NPF schemes capable of accurately predicting number concentrations of aerosols originated from nucleation processes, including their vertical profiles, without tuning factors (e.g. 10^{-5}) as is needed when using CNT-based NPF schemes?
4. How reliable are the extrapolation methods (based on aerosol dynamics) to estimate the particle formation rates of 3 nm particles (apparent formation rate) from measured formation rates of larger particles (e.g., 7 nm) for atmospheric NPF events?

2 Nucleation

Nucleation is defined as the initial step of transformation of one phase to another such as liquid-to-solid (crystallization), liquid-to-vapor (bubble formation) and, vapor-to-liquid (droplet formation; Seinfeld and Pandis (2006); Vehkamäki, 2006).

In this thesis, atmospheric particle formation by gas-to-particle conversion is our interest. The initial step of gas-to-particle conversion starts with transition of atmospheric precursors in their vapor phase (air) to the liquid (droplet) or solid phase. For this phase transition to happen, an energy barrier, which originates from creation of an interface between the gas and particle phases, needs to be overcome. The free energy of the new phase is lower than that of the initial phase. For nucleation to happen, the gas precursor is required to be supersaturated. The saturation ratio S_i describes the saturation degree of a vapor i in air at temperature T :

$$S_i = \frac{p_{i,v}}{p_{i,sat}(T)} \approx \frac{N_{i,v}}{N_{i,sat}(T)} \quad (1)$$

where $p_{i,v}$ and $N_{i,v}$ are the partial pressure and molecular number concentration of vapor i , respectively, and $p_{i,sat}(T)$ and $N_{i,sat}(T)$ are saturation vapor pressure and saturation molecular number concentration of i in equilibrium with its liquid phase at temperature T , respectively. Subsaturated, saturated and, supersaturated vapor is denoted by $S < 1$, $S = 1$ and, $S > 1$, respectively. At large enough S values, the cluster of vapor molecules (in air) experiences a competition of condensation and evaporation of vapor molecules, and, may grow to large enough size, so-called critical size, at which the monomer addition rate to the cluster is equal to the monomer loss rate. Below the critical size it is more probable for a cluster to shrink than grow. The clusters which exceed the critical size, however, most likely tend to grow rapidly and, in a way, complete the phase transition. The net number of clusters per unit time which grow past the critical size is called *nucleation rate*.

2.1 Classical Nucleation Theory (CNT)

The key foundations of classical nucleation theory were initiated in the 1930s by pioneers such as Volmer and Weber (1926), Farkas (1927) and Becker and Döring (1935). In the nucleation process an energy barrier required for the phase transition needs to be overcome by thermal energy. The nucleation theory predicts the probability of crossing this energy barrier as a Boltzmann factor $e^{-\Delta G/k_B T}$ where ΔG is the change in the Gibbs free energy (i.e. height of the energy barrier), k_B is Boltzmann's constant and T is the temperature.

ΔG includes contribution from the phase interface which is proportional to the surface area of the nucleus (assuming spherical shape) and bulk which is proportional to the volume of the nucleus:

$$\Delta G = 4\pi r_p^2 \sigma_p - \frac{4}{3}\pi r_p^3 \rho_p \frac{R^* T}{M_q} \ln S_q \quad (2)$$

where r_p is the radius (m), σ_p the surface tension (J m^{-2}) and ρ_p the mass density of the condensed cluster (kg m^{-3}), R^* is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), M_q is the molecular weight of condensing gas (kg mol^{-1}), and S_q is the saturation ratio of the gas. The nucleation rate ($\text{particles cm}^{-3} \text{s}^{-1}$) is:

$$J_{nuc} = C_{kin} e^{-\Delta G^*/k_B T} \quad (3)$$

where ΔG^* is the change in the Gibbs free energy to form the critical cluster (the maximum of ΔG) and C_{kin} ($\text{cm}^3 \text{s}^{-1}$) is a kinetic term, accounting for the collisions of vapor molecules with the cluster. CNT makes some important assumptions when defining ΔG . For example, a spherical shape is assumed for the clusters (which can contain only a few molecules). Another assumption is that CNT applies macroscopic values for the properties of the microscopic nucleus clusters. Even with its limitations, CNT has been widely used both to interpret laboratory experiments as well as in large-scale models to predict nucleation rates due to its convenience and reasonable computational cost. However, CNT-based approaches have failed to reproduce the measured particle formation/nucleation rates (Gaydos et al., 2005; Yu et al., 2006; Jung et al., 2006; Merikanto et al., 2007b; Zhang et al., 2010) which has resulted in the need to apply drastic correction factors (of the order of 10^{-5} to 10^{-6}) to the CNT-based formation rates to reproduce observed atmospheric number concentration profiles.

2.2 Nucleation mechanisms

Several nucleation mechanisms have been proposed to explain observations of atmospheric NPF:

2.2.1 CNT-based Binary and Ternary nucleation

Sulfuric acid (H_2SO_4) has a very low saturation vapor pressure in the presence of water vapor and thus tends to transform to the liquid phase by condensing or co-nucleating e.g. with water vapor which is abundant in atmosphere. Sulfuric acid is formed when sulfur dioxide (SO_2) is oxidized by OH radicals in the presence of water vapor. H_2SO_4 - H_2O nucleation (Doyle, 1961; Weber et al., 1999; Vehkamäki et al., 2002) is believed to be dominant nucleation mechanism in the upper troposphere. However, within the boundary layer at least a third species and even different mechanisms, seem to be involved. Ammonia (NH_3) has been recognized as another potentially important nucleation agent together with H_2SO_4 and H_2O through ternary H_2SO_4 - H_2O - NH_3 nucleation.

Full simulations of CNT as part of a large scale atmospheric model are computationally too heavy – thus the approach has been to perform a large set of CNT simulations separately, covering the atmospherically relevant parameter space, and parameterize the results through multidimensional curve-fitting. Such parameterizations of binary and ternary nucleation have been proposed e.g. by Vehkamäki et al. (2002) and Napari et al., (2002), respectively. For the case of ternary H_2SO_4 - H_2O - NH_3 nucleation, the latter parameterization has been found to produce tropospheric nucleation rates, and consequently particle number concentrations that are dramatically higher than observations. Thus there has been a need to apply a correction factor (10^{-5} or 10^{-6}) to the predicted rates.

More recently, amines have been found as another candidate to co-nucleate with H_2SO_4 and H_2O by both quantum chemical calculations and laboratory works (Kurten et al., 2008; Berndt et al., 2010; Erupe et al., 2011; Zollner et al., 2010; Almeida et al., 2013). A molecular analysis of the sulfuric acid

amine clusters has revealed that the enhancing effect on nucleation is explained by a base-stabilization mechanism involving acid–amine pairs, which strongly decreases evaporation (Almeida et al., 2013).

2.2.2 Semi-empirical approach

McMurry and Friedlander (1979) and McMurry (1980) proposed a kinetic nucleation mechanism indicating that collisions of sulfuric acid monomers produce stable dimers and thus there is no thermodynamic energy barrier for nucleation.

Several observations have revealed that the nucleation rates correlate with sulfuric acid concentration (e.g. Weber et al., 1996; Birmili et al., 2000; Fiedler et al., 2005; Kulmala et al., 2006; Sihto et al., 2006; Riipinen et al., 2007). The dependence of the atmospheric nucleation rate on sulfuric acid can be typically approximated by a power-law:

$$J_{nuc} \propto [H_2SO_4]^n \quad (4)$$

where the power-law exponent $1 \leq n \leq 2$. The CNT-based binary and ternary nucleation predict that $n > 10$ and $5 < n < 10$ (e.g. Bernd et al., 2005), respectively. The kinetic type nucleation, originating from the ideas of McMurry and Friedlander (1979) with $n = 2$, is based on kinetic gas theory, assuming that collisions between sulfuric acid molecules or molecule clusters containing sulfuric acid lead to new stable clusters. Kinetic nucleation rate is thus given by $J_{nuc} = K [H_2SO_4]^2$ where the coefficient K then includes e.g. molecular properties, possible effect on conditions and the probability that a monomer collision results in forming a stable cluster.

Ion-mediated nucleation has been proposed (Yu and Turco, 2000) as another mechanism of atmospheric nucleation. Ions are continuously added to atmosphere through ionization by Galactic Cosmic Rays (GCR) or other localized sources such as combustion, lightning, corona discharge, etc. Stable clusters can be formed for example by ion-ion recombination or ion-neutral reaction. Ions are considered to have a relatively small overall role in the atmospheric nucleation process (e.g. Bianchi et al., 2016). Very recently, however, Kirkby et al., (2016) set up an experiment in which Highly Oxygenated Molecules (HOMs; produced by ozonolysis of α -pinene) were exposed to ions generated by GCR. They observed nucleation without the presence of sulfuric acid and, furthermore, found out that ions can increase the nucleation rates of these biogenic HOM-clusters by one to two orders of magnitudes compare to neutral nucleation (ion-free). Therefore, if these observations in a well-controlled chamber represent also real atmospheric conditions, tropospheric nucleation could be described by two major distinct mechanisms. First, the ternary H_2SO_4 - H_2O - x which correlates with the H_2SO_4 concentration. The stabilizing species x can be e.g. ammonia, amines or HOMs or a combination of these. The second mechanism, suggested by Kirkby et al. (2016), could only be dominant in pristine environments with very low sulfuric acid concentration and involves the nucleation of pure organic vapors with ions and oxidized organic vapors as the stabilizing agents. In a

very recent paper, Gordon et al. (2016) found that by implementing the parameterized HOM nucleation mechanism of Kirkby et al (2016) the baseline preindustrial aerosol concentration is higher than thought before and could lead to a reduction of 27% in estimates of anthropogenic aerosol radiative forcing.

2.3 Dynamical processes of nuclei

2.3.1 Condensation

Diffusion of a vapor to the surface of nucleated particles which involves a gas phase change of the diffusing gas is called *condensation*. The vapors condensing on the clusters need to have a low enough equilibrium vapor pressure (with respect to the condensed phase) so that they stay in their condensed phase. The vapors responsible for condensational growth can be either species involved in the nucleation itself (e.g. sulfuric acid, ammonia, amines, water vapor) or different from those. Organic vapors like Volatile Organic Compounds (VOC) mostly emitted from trees and vegetation can also grow the nuclei after they have been oxidized (by OH, O₃ and NO₃) and thus become of low volatile enough. Isoprene, monoterpenes and sesquiterpenes are the main biogenic VOCs. In situ measurements have shown that organic compounds are a major fraction of atmospheric aerosols (Jimenez et al., 2009; Zhang et al., 2011).

The driving force behind condensation is the difference between the vapor pressure (or concentration) of the condensing vapor at the particle surface (denoted by p_{eq} (Pa) and C_{eq} (cm⁻³)) and far from particle surface (p_{vapor} (Pa) and C_{vapor} (cm⁻³); Seinfeld and Pandis, 2006). Therefore, the direction and magnitude of the flux of condensing vapor towards/from the particle surface is proportional to $(p_{vapor} - p_{eq})$ or $(C_{vapor} - C_{eq})$.

As mentioned earlier, sulfuric acid has a very low vapor pressure in the presence of water vapor thus tends to participate in nucleation and condensational growth. The rate of change in the sulfuric acid concentration in the atmosphere (Pierce and Adams, 2009) can be estimated from:

$$\frac{d[H_2SO_4]}{dt} = P_{H_2SO_4} - CS \cdot [H_2SO_4] - J_{nuc} \cdot M_{nuc} \quad (5)$$

where $[H_2SO_4]$ is the concentration (cm⁻³) of gas-phase sulfuric acid, $P_{H_2SO_4}$ (cm⁻³ s⁻¹) is the chemical production rate of sulfuric acid vapor via reaction of sulfur dioxide SO_2 and OH radicals, CS is the condensation sink that accounts for the loss rate of sulfuric acid vapor to pre-existing aerosols with the unit s⁻¹, J_{nuc} (cm⁻³ s⁻¹) is the nucleation rate and M_{nuc} is the amount of the sulfuric acid consumed in one single nucleation process.

The condensation sink CS is an important parameter that indicates how rapidly the condensing vapor molecules with diffusion coefficient D_{vapor} ($\text{cm}^2 \text{s}^{-1}$) and mean free path λ_{vapor} (cm) condense onto pre-existing particles with number distribution $n(d_p)$ (Kulmala et al., 2001):

$$CS = 2\pi D_{vapor} \int_0^{\infty} d_p \beta(d_p, \alpha) n(d_p) dd_p = 2\pi D_{vapor} \sum_i^n \beta_{M_i} d_{p,i} N_i \quad (6)$$

The transitional correction factor β extrapolates the continuum regime ($Kn = \frac{2\lambda_v}{d_p} < 1$) condensation theory to the transition and free molecular regimes ($Kn = \frac{2\lambda_v}{d_p} > 1$). A widely used equation for β is the one derived by Fuchs and Sutugin (1970):

$$\beta = \frac{Kn + 1}{0.377Kn + 1 + \frac{4}{3}Kn^2 \alpha^{-1} + \frac{4}{3}Kn \alpha^{-1}} \quad (7)$$

where α is the sticking coefficient or the mass accommodation coefficient which is usually assumed to be unity (Winkler et al., 2004). To take into consideration the hygroscopic growth of particles due to uptake of water vapor, a growth factor (GF) which is RH and particle-size dependent is applied to the particles size bins. In our study, we adopted the GF function from Laakso et al., (2004).

2.3.2 Coagulation

Coagulation of aerosol particles is defined as a collision of particles which make them sticking together. The collisions can be induced by Brownian diffusion, electrostatic forces, gravitational settling. In this thesis the focus is on Brownian coagulation as it is the most dominant coagulation process for sub-micron particles in the atmosphere.

When new particles have formed and start to grow, they may collide with existing larger particles and are thus removed from the gas. The coagulation sink ($CoagS$) gives the rate by which the nm-sized particles are lost to the existing larger particles and is calculated as follows (Kulmala et al., 2001; Seinfeld and Pandis, 2006):

$$CoagS(d_{p,i}) = \sum_j K_{i,j}(d_{p,i}, d_{p,j}) N_j \quad (8)$$

where $K_{i,j}$ is the coagulation coefficient of particles in i^{th} and j^{th} size classes. The coagulation coefficient $K_{i,j}$ of two colliding particles in size classes i and j with diameter $d_{p,i}$ and $d_{p,j}$, diffusion coefficients D_i and D_j , and the mean thermal velocities \bar{c}_i and \bar{c}_j is given by:

$$K_{i,j} = \frac{2\pi(d_{p,i} + d_{p,j})(D_i + D_j)}{\frac{d_{p,i} + d_{p,j}}{d_{p,i} + d_{p,j} + 2\sigma_{i,j}} + \frac{4(D_i + D_j)}{(d_{p,i} + d_{p,j})\bar{c}_{i,j}}} \quad (9)$$

where $c_{i,j}$ is the relative thermal velocity of two coagulating particles.

3 After nucleation: New-Particle Formation (NPF) process

After the stable molecule clusters have been formed with a size of around 1 nm in diameter, they may start to grow by condensation to larger sizes. However, they can also be lost by coagulation with pre-existing particles or by other removal processes such as wet and dry deposition. Some of these growing particles survive these scavenging processes and grow to sizes where they can be detected e.g. by Differential Mobility Particle Sizer (DMPS) or Scanning Mobility Particle Sizer (SMPS). This process of nucleation and subsequent growth is known as new-particle formation (NPF). The scavenging rate by coagulation onto larger particles is decreasing with increasing particle size and a significant fraction of those particles that grow to detectable sizes (typically 3 nm) grow further past 50 nm where they can serve as cloud condensation nuclei (CCN).

3.1 Aerosol size distribution

Atmospheric aerosols are characterized by their concentration (typically number, mass and/or surface area), size distribution, and chemical composition. In this thesis, the number distribution of submicron particles is especially important because of its important role both in climate and human health (Ahlm et al., 2013). The number of cloud condensation nuclei (CCN) and furthermore cloud activation as well as the fraction of particle pollution penetrating the human lung are estimated primarily from the aerosol number size distribution.

The size distribution of submicron particles can be typically quite well described by a sum of several log-normal distributions (Whitby 1978, 1987, 1991; Mäkelä et al. 2000; Birmili et al. 2001; Hussein et al., 2004, 2005). In the case of discrete distributions, the particle size distribution is represented as

discrete bin concentrations (in particles cm^{-3}). The total number concentration is then obtained by summing the concentrations in all size bins.

Dynamical processes change the aerosol size and chemical composition distribution. These processes include nucleation, condensation, coagulation, evaporation, wet and dry deposition, aqueous chemistry, and aerosol-cloud interactions. An integro-differential equation describing the rate of change of the particle size distribution function $n(v, t)$ ($\mu\text{m}^{-3} \text{cm}^{-3}$) due to these aerosol dynamical processes can be derived. This equation is called the General Dynamical Equation (GDE), here expressed in terms of particle volume v (μm^{-3}) (Gelbard and Seinfeld, 1979; Seinfeld and Pandis, 2006):

$$\begin{aligned} \frac{\partial n(v, t)}{\partial t} = & \frac{1}{2} \int_0^v K(v - q, q) n(v - q, t) n(q, t) dq - n(v, t) \int_0^\infty K(q, v) n(q, t) dq \\ & - \frac{\partial}{\partial v} [I(v) n(v, t)] + J_{nuc} \delta(v - v_{nuc}) + S(v) - R(v), \end{aligned} \quad (10)$$

where t (s) is time, $K(q, v)$ ($\text{cm}^3 \text{s}^{-1}$) is the coagulation coefficient between particles of volume q and v , $I(v)$ ($\mu\text{m}^3 \text{s}^{-1}$) is the condensational volume flux, J_{nuc} ($\text{cm}^{-3} \text{s}^{-1}$) is nucleation rate, $\delta(v - v_{nuc})$ is the Dirac delta function which is equal to infinity if $v = v_{nuc}$, with v_{nuc} being the volume of nucleus, and zero elsewhere, $S(v)$ and $R(v)$ are other possible source and sink terms. The first two terms on the right hand side represent the formation and loss of particles by coagulation (as the dominant loss process for atmospheric particles), the third condensation/evaporation and the fourth nucleation.

3.1.1 Techniques to measure the aerosol number concentration

Optical and electrostatic methods are commonly used for sizing the aerosol particles and measuring their number concentration. DMPS has been long used to measure the size distribution. Until very recently the measurement range of DMPS has been limited to particle size above 3 nm in diameter. In DMPS, particles are first artificially neutralized (in order to reach a well-defined charge distribution) and then exposed to an electric field within a Differential Mobility Analyzer (DMA) for size classification based on their electrical mobility. The electrical mobility (B_e) of a particle with electrical charge q is given by (Seinfeld and Pandis, 2006):

$$B_e = \frac{qC_c}{3\pi\mu D_p}, \quad (11)$$

where D_p is the particle mobility diameter, C_c is the Cunningham slip correction factor, which depends on particle diameter, and μ is air viscosity. After sizing by DMA, the concentration of particles is measured by Condensation Particle Counter (CPC). CPC enlarges particles by condensation of supersaturated vapor (most often butanol, sometimes water), to sizes where they can be optically detected. In **Paper I and III**, we use the particle number size distributions measured by twin-DMPS

systems at Hyytiälä (Finland), Puijo (Finland) and San Pietro Capofiume (SPC, Italy). A twin-DMPS consists of two DMAs covering two different size ranges and two CPCs. In Paper II, we again make use of the ground-level particle number size distributions measured by DMPS at several different European sites including Hyytiälä. We also use the vertical profiles of particle number concentration measured by PCASP-100X (Passive Cavity Aerosol Spectrometer Probe; Liu et al., 1992) and CPSA (Condensation Particle Size Analyzer; Fiebig et al., 2005; Feldpausch et al., 2006). PCASP-100X is an airborne optical spectrometer which measures the number concentration of accumulation-sized particles, and sizes the particles based on the intensity of the light scattered by the particles. CPSA consists of four CPCs which count the number of particles at different cut-off diameters (the values of which depend on the supersaturation reached in the instrument). We used the measurements covering the size range 160-1040 nm from the channels 3 to 10) of PCASP and two channels of CPSA with lower cut-off diameters 4 and 10 nm (**Paper II**).

3.2 Characteristics of NPF events

NPF events are commonly detected from the evolution of measured particle number size distributions in terms of their number concentration. Figure 1 shows three examples of NPF event days observed in Hyytiälä, Finland (Figure 2 in **Paper III**). As can be seen from the figure, a burst in number concentration of small particles (nucleation mode) appears around noon, which further grow, to larger sizes (Aitken and Accumulation modes) where they become climatologically important.

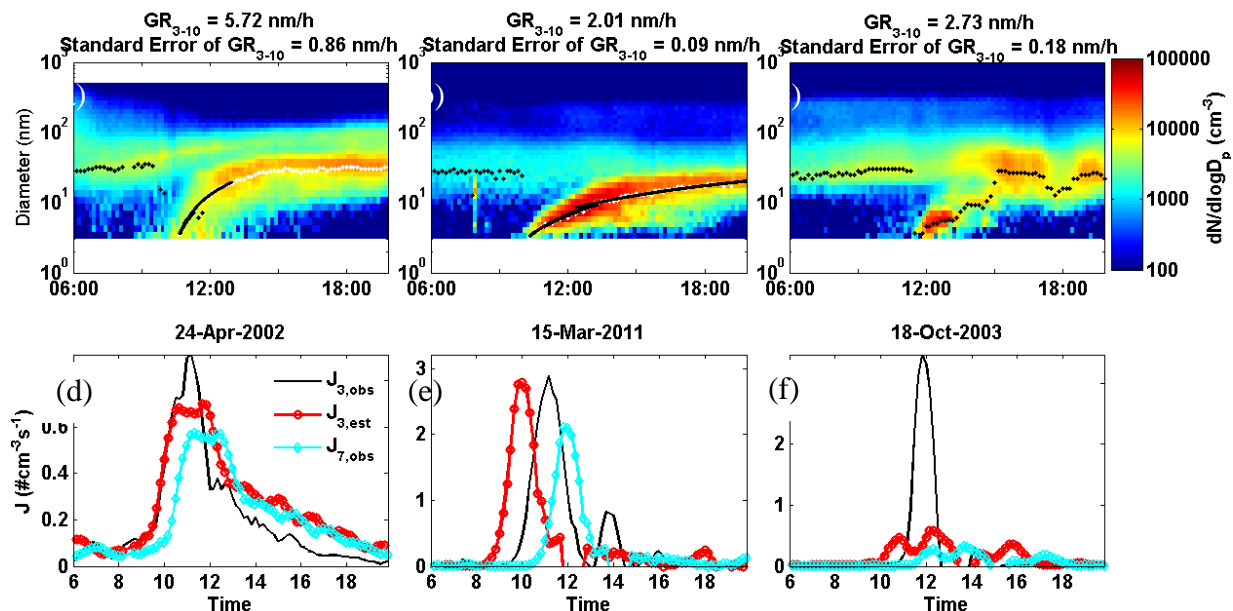


Figure 1: Examples of Hyytiälä NPF events. Figures (a, b, and c) present the evolution of the particle number size distributions measured by DMPS. White dots represent the geometric mean diameters that corresponds to the peak value of the individual fitted lognormal functions, and the solid black line

shows the first-order polynomial fit. Figures (d, e, and f) show the corresponding evolution of 3 nm particle formation rates obtained from Eq. (4) in **Paper III** (red), observed $J_{3,obs}$ (black) and observed formation rates of 7 nm particles $J_{7,obs}$ (cyan).

The basic characteristics of NPF events are their nucleation rate, particle formation rate and growth rate ($GR = \frac{dd_p}{dt}$). Nucleation rate or “actual” formation rate refers to the formation rate of sub-2-nm nuclei and is typically a challenging task to measure. The “particle-formation rate” or so-called “apparent” formation rate of NPF events (see the curves in Figure 1-d-e-f) describes the formation rate of nuclei at a larger, or measurable, size (typically at 3 nm or above) for which there exists established measurement techniques. Several studies have suggested extrapolation methods to determine the actual nucleation rates from measured formation rates (McMurry and Friedlander (1979); McMurry (1982; 1983); Weber et al. (1996); Kerminen and Kulmala (2002); Kerminen et al. (2003); Lehtinen et al. (2007); Kürten et al. (2015)). In **Paper III**, we used the method by Lehtinen et al. (2007), which is a follow up study of Kerminen and Kulmala (2002), to extrapolate the formation rates of 7-nm particles down to formation rate of 3-nm particles in Puijo (Finland). Particle number size distributions measurements extend only down to 7 nm in Puijo. To validate the method, we applied it first on NPF events observed and quantified in Hyytiälä (see examples in Figure 1). The key assumptions in the method by Lehtinen et al. (2002) are that 1) nuclei are lost only by coagulation onto larger particles, with a coagulation sink that has a power-law dependence on nuclei diameter, 2) nuclei grow by condensation with a constant GR, 3) the background particle population remains unchanged during growth (Figure 2).

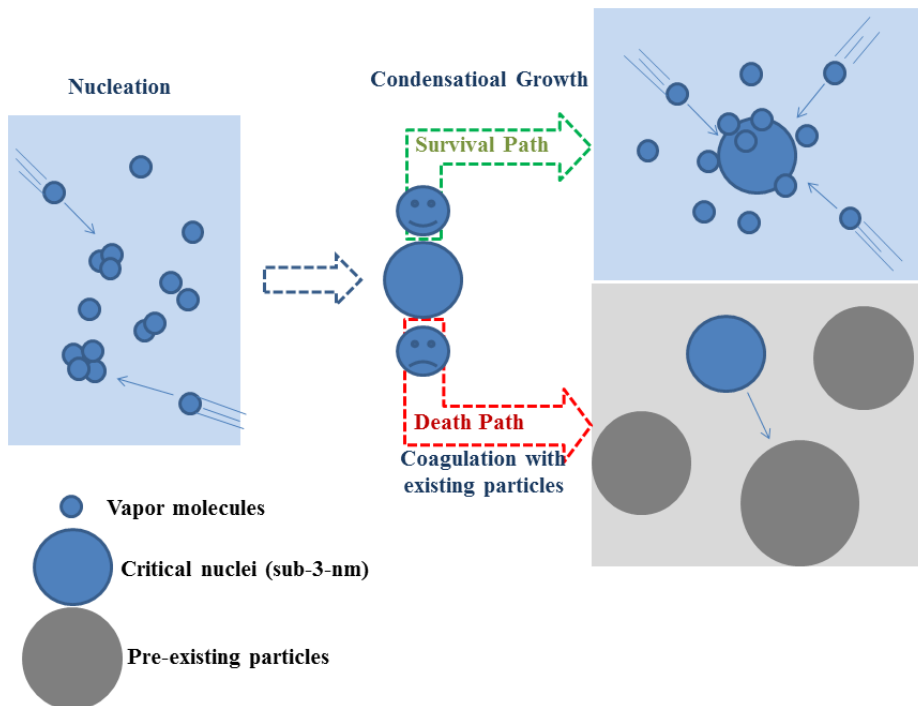


Figure 2: Nucleation, growth, and coagulation scavenging of atmospheric nuclei.

Therefore, the change in number concentration of nuclei within size range $[d_1, d_2]$ is determined by those dynamic processes which result in loss or production of new particles:

$$\frac{dN_{[d_1, d_2]}}{dt} = \text{production rate} - \text{loss rate} = J_{d_1} - J_{d_2} - N_{[d_1, d_2]} \cdot \text{CoagS} \quad (12)$$

where J_{d_1} and J_{d_2} can be interpreted as apparent formation rates of particles at the lower and upper limits of the size range, respectively. Actually, J_{d_1} is the flux of growing particles into the size range at the lower limit while J_{d_2} is the flux of particles that grow out of the size range. The term $N_{[d_1, d_2]} \cdot \text{CoagS}$ describes the loss of particles within the size range due to their coagulation with larger background particles.

In a continuous description of aerosol dynamics the formation rate J can be written as

$$J = \frac{dd_p}{dt} \cdot n(d_p) = GR \cdot n(d_p) \text{ where } n \text{ is the aerosol size distribution } n = \frac{dN}{dd_p}. \text{ Using equation (10)}$$

and the assumptions mentioned earlier, Lehtinen et al. (2007) derived an expression by which the formation rate of the particles at lower limit of the size range $[d_1, d_2]$ can be estimated from the formation rate of particles of the upper limit (J_{d_2}), and vice versa, from:

$$J_{d_1} = J_{d_2} \cdot \exp\left(\gamma \cdot d_1 \cdot \frac{\text{CoagS}(d_1)}{GR}\right), \quad (13)$$

$$\text{with } \gamma = \frac{1}{m+1} \left(\left(\frac{d_2}{d_1}\right)^{m+1} - 1\right) \text{ and } m = \frac{\log[\text{CoagS}(d_2)/\text{CoagS}(d_1)]}{\log[d_2/d_1]},$$

To obtain the equation it is assumed that the growth rate of particles is size and time independent ($GR = \text{constant}$), and that the coagulation sink is time independent but power-law size dependent:

$$\text{CoagS}(d_2) = \text{CoagS}(d_1) \left(\frac{d_2}{d_1}\right)^m,$$

where m is obtained directly from the background particle number size distributions, and is typically in the range $[-2, -1.5]$.

To determine the growth rate, two methods have commonly been used. In the so-called maximum-concentration method (Lehtinen and Kulmala, 2002); at a given diameter the maximum particle concentration during the time of measurement is determined and a growth rate is then determined by linear fit to the peak times and corresponding diameters. Other approach is through mode-fitting; at a given measurement scan (usually by DMPS) a log-normal mode is fitted to the nucleation mode and then the growth rate is determined by a linear fit to the time evolution of the geometric-mean diameter. In **Paper III**, we have used the latter method, with the automated algorithm developed by Hussein et al. (2005) for fitting log-normal modes to the measured size distributions (black dots and white fitted line in Figure 1).

3.3 Simulation of NPF process

3.3.1 3-D regional-scale chemical-transport model PMCAMx-UF description

The three-dimensional regional chemical transport model (CTM) PMCAMx-UF, an extension of the air quality model PMCAMx (Gaydos et al., 2007, Karydis et al., 2007), simulates both the size-dependent particle number and chemically resolved mass concentrations (Jung et al. 2010). Comprehensive Air Quality Model with Extensions (CAMx) is the framework of PMCAMx (thus PMCAMx-UF), which describes the vertical and horizontal advection and dispersion, wet and dry deposition, and gas-phase chemistry. The main difference in PMCAMx-UF as compared with PMCAMx, is in treating the aerosol microphysics, including NPF, condensation and coagulation done by Dynamic Model for Aerosol Nucleation (DMAN) module by Jung et al. (2006; see also Figure 3). DMAN uses the Two-Moment Aerosol Sectional (TOMAS) algorithm (Adams and Seinfeld, 2002) to track the aerosol number and mass distributions. DMAN divides the aerosol particles into 41 logarithmically-spaced size bins between 0.8 nm and 10 μm . **Paper II** and papers cited in this section, describe the PMCAMx-UF model in more detail.

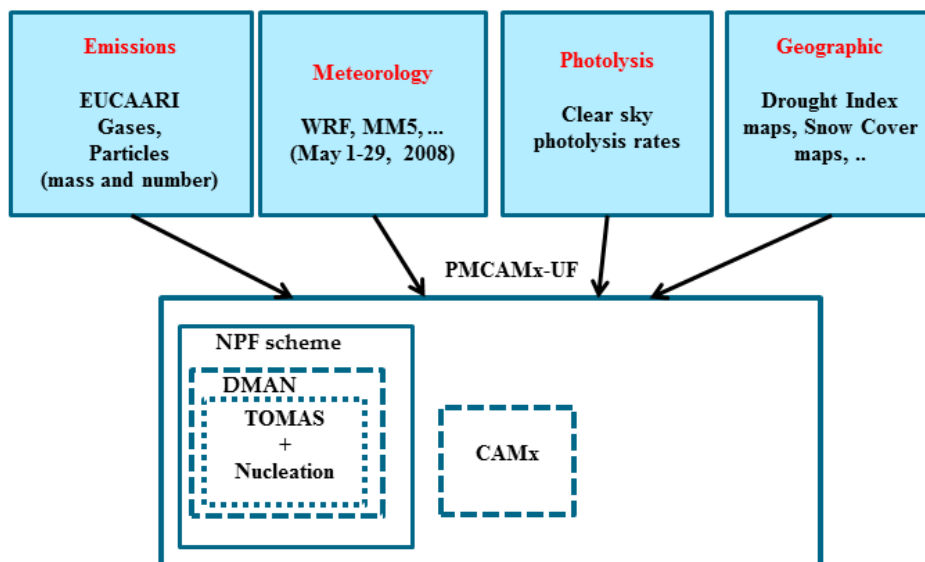


Figure 3: Schematic description of PMCAMx-UF. Note that NPF process is only one of the many other processes implemented in PMCAMx-UF (inspired by CAMx's user guide, version 6.40; http://www.camx.com/files/camxusersguide_v6-40.pdf).

3.3.2 NPF schemes in PMCAMx-UF

The balance equation of the aerosol number and mass concentrations (C_j) is generally described as follows (Jung et al., 2006):

$$\frac{dC_j}{dt} = R_{nuc} + R_{cond} + R_{coag} \quad (14)$$

where R_{nuc} , R_{cond} , R_{coag} (units are particles $\text{cm}^{-3} \text{s}^{-1}$ and $\mu\text{g cm}^{-3} \text{s}^{-1}$ for number and mass concentrations, respectively) are the nucleation, condensation and coagulation rates.

Nucleation rates are calculated within the DMAN module using the ternary nucleation ($\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$) parameterization by Napari et al. (2002) and the binary nucleation ($\text{H}_2\text{SO}_4\text{-H}_2\text{O}$) parameterization by Vehkamäki et al. (2002), which both are CNT-based schemes. In DMAN, ternary nucleation is on when the sulfuric acid and ammonia concentrations exceed $10^4 \text{ molec cm}^{-3}$ and 1ppt, respectively. Otherwise, the binary pathway is on (as long as sulfuric acid concentration exceed $10^4 \text{ molec cm}^{-3}$). In **Paper II**, we updated the ternary nucleation pathway with the nucleation rates simulated by the Atmospheric Cluster Dynamics Code (ACDC, McGrath et al., 2012; Olenius et al., 2013; Almeida et al., 2013; Henschel et al., 2015) which is based on first-principle calculations of nucleation.

ACDC simulates the kinetic of the molecular cluster population by numerically solving the birth-death equations of clusters (McGrath et al., 2012; Olenius et al., 2013). The main processes that result in generation of a given cluster is collision of smaller clusters and fragmentation of larger clusters, while destruction of the clusters takes place due to the fragmentation of the given cluster and coagulation with other larger clusters. One of the benefits of the ACDC code is its flexibility to calculate or input the Gibbs free energies values of clusters formation (to calculate the evaporation rates) from any method. Quantum chemical input data used in ACDC has been proven as a suitable method to calculate the free energies (Almeida et al., 2013) instead of the liquid droplet model used in the CNT approach (Merikanto et al., 2007a). Another strength of ACDC is that, unlike in CNT, collisions and evaporation of di- and higher mers are taken into account. The clusters (approximately 1.3 nm in mobility diameter) simulated by ACDC in Paper II contain up to three sulfuric acid and three ammonia molecules which are hydrated by up to five water molecules. The flux of clusters growing out of the tracked system determines particle formation rates in steady-state (Henschel et al., 2015).

3.4 Solar radiation and cloudiness effects on NPF events

The precursor gases involved in nucleation and subsequent growth of nuclei undergo photochemical reactions and become oxidized with radical species in the atmosphere. The radical production rate in turn is strongly correlated with the solar radiation intensity, in particular the UV light intensity. The hydroxyl radicals ($\text{OH}\cdot$) are responsible for oxidation of most atmospheric compounds and pollutants

(Bonn et al., 2014; Gligorovski et al., 2015) such as sulfur dioxide SO_2 which results in sulfuric acid production. Therefore, the sulfuric acid concentration is strongly correlated with the OH concentration and with the solar radiation intensity. Thus, any change in radiation intensity will affect the new-particle formation process. Clouds, for example, affect the photolysis rates of photochemical reactions by influencing the incoming solar radiation. Clouds can both attenuate and enhance the solar radiation, in particular the actinic flux of ultraviolet (UV) and visible radiation, which are responsible for photolysis. The enhancement of actinic flux above cloud is due to the increased reflection (from clouds) of solar radiation. In addition, clouds in clean environments affect NPF, because of their cleansing effect, which leads to lowering the condensation sink (or aerosol surface concentration) (Shaw 1989; Wehner et al., 2015). Most recently, Wehner et al., (2015) observed NPF enhancement near the cloudy regions due to increased irradiance (**Paper II**) in the UV spectrum. They concluded that, this (i.e. enhancement of NPF in the vicinity of clouds with increased irradiance) could be intensified by increased turbulence in the cloud edges as well as mixing with cleaner air leading to a lower condensation sink. In addition, dimethyl sulfide can be brought up with cloud updrafts to the cleaner cloud layer where it becomes oxidized to SO_2 and H_2SO_4 . This, requires enhanced radiation to produce precursors for NPF (Wehner et al., 2015).

3.4.1 Cloud-adjustment to photolysis rates in PMCAMx-UF

The Regional Acid Deposition Model (RADM; Chang et al., 1987) is used in PMCAMx-UF to treat the effect of cloudiness on photolysis rates. RADM uses the cloud optical depth from the meteorological input data and the solar zenith angle to estimate the time- and layer-dependent adjustment factors (A_{adj}) for the photolysis rates ($J_{apparent} = A_{adj} J_{clear}$). In **Paper II**, we replaced RADM with TUV (Tropospheric Ultraviolet and Visible radiative-transfer model; Madronich, 2002). In contrast to RADM approach, the TUV model accounts for the direct effect of aerosols and particulate water. TUV also represents the scattering of shortwave radiation that could happen between cloudy layers and between the cloud and ground.

3.4.2 Determination of cloudiness from measured solar radiation

In **Paper I**, we calculated the relative solar radiation intensity (I/I_{max}), in which I is the measured global radiation intensity ($W\ m^{-2}$) and I_{max} the maximum possible radiation intensity corresponding to cloud- and aerosol-free conditions. I/I_{max} , therefore, indicates the fraction of incoming radiation reached to ground after being attenuated by clouds and aerosols and is therefore also a measure of cloudiness. The motivation behind our interest in the ratio I/I_{max} was that we first tried to unsuccessfully correlate I with NPF, but quickly found out that the absolute radiation intensity I alone cannot explain the occurrence of NPF days because of the natural annual variation in I_{max} . Especially,

there are several non-event days in the summer when the daily mean radiation intensity I is higher than on the event days occurring during the other seasons (Figure 3 in Paper I).

4 Main Results and Conclusions

The main findings of this thesis are summarized below in chronological order and as responses to the scientific questions mentioned in the introduction section (see the Introduction section).

Response to Question 1 (Paper I)

Analysis of relative radiation intensity (Paper I) showed that NPF was more probable on days with clear sky conditions than on days with cloudy skies. This was the case even if the absolute radiation intensity on cloudy days (usually in summer) would be higher than on some of the clear sky days (usually in winter or spring). This is possibly because clouds block UV radiation more efficiently than visible light - thus the UV intensity on e.g. a clear winter/spring day may be higher than on a cloudy summer day even if the intensity of visible light is lower. Thus, radiation intensity alone is not a good enough predictor for NPF. Instead, the relative global radiation intensity, i.e. the ratio of the radiation intensity to the maximum possible radiation intensity during that day was shown to be a somewhat better variable. This became clear after analyzing the arithmetic daily-mean values of global radiation intensity (measured) and maximum possible radiation intensity (modeled) of NPF events and non-events (Figure 3 in **Paper I**) in Hyytiälä (Finland) and San Pietro Capofiume (SPC, Italy). Further analysis showed that most of the NPF events are associated with high relative radiation intensity values and thus clear sky conditions. Approximately, 60 % of the days with high relative radiation intensity (0.9-1) in Hyytiälä (2002-2012) were NPF event days, while most days with lower relative radiation intensity were non-event days. A low condensation sink and a high sulfur dioxide concentration explain the anomalous NPF days (mostly weak NPF events) taking place at cloudy conditions. Opposite conditions are characteristic for the anomalous non-events at clear sky conditions. The ‘normal’ NPF event days (at clear sky conditions) are characterized with a low relative humidity and a high SO₂ concentration.

Response to Question 2 (Paper II)

Changing the cloud-adjustment scheme from RADM parametrization to radiative transfer module TUV revealed enhancement of new particle formation near cloudy regions, which, however, had only a small effect on predicted total particle number concentrations (Paper II). We depicted (**Paper II, Figure 5**) the absolute difference between predictions using both the base model (i.e. PMCAMx-UF with RADM as radiation scheme) and the model with the TUV radiation scheme of sulfuric acid and particle number concentrations along with cloud optical depth. The sulfuric acid concentration is increased near cloudy regions due to enhanced photolysis rates driven by enhanced UV radiation, which thus results in increased new particle formation. Below cloud, however, the particle number and sulfuric acid concentrations are decreased due to attenuation of UV radiation.

Response to Question 3 (Paper II)

The first principles-based NPF scheme *using ACDC, is a promising tool to predict atmospheric aerosol number concentrations with reasonable accuracy without using any empirical correction factor.* Findings of **Paper II** suggest that reliance on parameterizations of inaccurate classical nucleation theories (CNT), which for a long time have been used in large-scale aerosol-climate models (due to low computational cost) can gradually come to an end. The number concentrations of particles larger than 4 nm (N_4) and 10 nm (N_{10}) and within the size range 160-1040 nm ($N_{160-1040}$), predicted by PMCAMx-UF with the ACDC-based NPF scheme, were validated against aircraft measurements. The predicted vertical profile of N_4 is within one order of magnitude of observations. This is encouraging considering the fact that, in comparison, a correction factor of 10^{-6} has been widely used together with the ternary CNT scheme in order to obtain reasonable results. Predictions of number concentrations of larger particles including Aitken and accumulation modes by the PMCAMx-UF with ACDC-based NPF scheme, are generally in good agreement with the observations (see **Paper II** for details). The $N_{160-1040}$ vertical profile is underpredicted by about a factor of five regardless of the NPF scheme (i.e., CNT-based or ACDC-based). We believe that including organic condensation, which is not included in the current version of the model, can improve the predictions of the number concentration of small particles even further. The same holds also for ground-based predictions of particle number concentrations; the ground-based hourly-averaged N_{10} , N_{50} , and N_{100} predictions were compared to the measurements collected during the EUCAARI campaign over various European countries. It is shown that while the predictions are generally in good agreement with observations the N_{10} and N_{100} are slightly over- and under-predicted, respectively.

Response to Question 4 (Paper III)

Extrapolating particle formation rates from one measured larger size (e.g. 7 nm) to smaller sizes (e.g. 3 nm) based on simplified growth-scavenging dynamics works fairly well to estimate mean daily particle formation rates, but fails to predict the time evolution of the particle population (**Paper III**). Using the analytical formula by Lehtinen et al. (2007), formation rates of 3 nm particles (J_3) for the NPF events at SMEAR IV station in Kuopio, Finland, were estimated. This was done by scaling the measured formation rates of 7 nm particles (i.e. cut-off size of DMPS in Puijo). The method was first evaluated using NPF events at SMEAR II station in Hyytiälä, Finland, where the estimated formation rates can be compared to directly measured 3 nm particle formation rates. Testing the analytical method of Lehtinen et al. (2007) using atmospheric measured data, for the first time, reveals the strength of the method in estimation of event mean values of 3-nm particle formation rates (J_3) from scaling the measured J_7 . This is reflected from scatter plots of the mean values of estimated J_3 ($J_{3,est}$) versus measured J_3 ($J_{3,obs}$). The 10-minute $J_{3,obs}$ and $J_{3,est}$ values, however, are poorly correlated indicating the failure of the formula of simulating the daily evaluation of particle formation rates. The reason for this is due to the fact that there is a time lag between J_3 and J_7 , and failure to predict this time lag through estimating the growth rate is to blame. This points to the challenges in predicting atmospheric nucleation rates for locations where the particle growth and loss rates are size and time-dependent.

5 The author's contribution in papers

Paper I The author took the lead of the research and carried out the data analysis, interpreting the results, and wrote the paper. Prof. Ari Laaksonen and Dr. Antti Arola provided frequent advice and regular meetings and commented on the paper.

Paper II This work involved collaboration with the Stockholm University, with supervision of Assoc. Prof. Iiona Riipinen and the postdoc fellows at her group Dr. Benjamin Murphy and Dr. Jan Julin. Aforementioned colleagues at Stockholm University as well as Prof. Kari Lehtinen from University of Eastern Finland provided frequent advice and regular meetings. The author wrote the results and method section of the paper. The paper includes two phases:

Phase (1) the author contributed in implementing the new radiation scheme within the PMCAMx-UF model, performed the model simulations, and post-processed and analyzed the model outputs.

Phase (2) the new NPF scheme was implemented by Dr. Jan Julin and Dr. Benjamin Murphy. The author carried out post-processing and analyzing the model outputs.

Paper III The author analyzed the data and wrote the paper. Prof. Kari Lehtinen and Dr. Tuomo Nieminen provided frequent advice and regular meetings.

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