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Modelling the formation of organic particles in the atmosphere

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Abstract

A modelling study investigating the formation of organic particles from inorganic, thermodynamically stable clusters was carried out. A recently-developed theory, the so-called nano-Köhler theory, which describes a thermodynamic equilibrium between a nanometer-size cluster, water and water-soluble organic compound, was implemented in a dynamical model along with a treatment of the appropriate aerosol and gas-phase processes. The obtained results suggest that both gaseous sulphuric acid and organic vapours contribute to organic particle formation. The initial growth of freshly-nucleated clusters having a diameter around 1 nm is driven by condensation of gaseous sulphuric acid and by a lesser extent cluster self-coagulation. After the clusters have reached sizes of around 2 nm in diameter, low-volatile organic vapours start to condense spontaneously into the clusters, thereby accelerating their growth to detectable sizes. A shortage of gaseous sulphuric acid or organic vapours limit, or suppress altogether, the particle formation, since freshly-nucleated clusters are rapidly coagulated away by pre-existing particles. The obtained modelling results were applied to explaining the observed seasonal cycle in the number of aerosol formation events in a continental forest site.

1. Introduction

As was recently highlighted by the Intergovernmental Panel on Climate Change (IPCC), interactions of aerosols with the atmosphere need to be quantified in order to assess reliably the impact of anthropogenic activities to the climate (IPCC, 2001). This is necessitated by the fact that aerosols exert a strong effect on the radiative properties of the atmosphere by scattering incoming solar radiation and by acting as cloud condensation nuclei, thereby modifying the cloud albedo and lifetime. These effects depend considerably on the number concentration of atmospheric aerosol populations along with their size and chemical composition. Due to this sensitivity, a realistic treatment of

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the aerosol-climate interactions in global climate models requires accurate knowledge on different source mechanisms for atmospheric aerosols.

Aerosols are produced in the atmosphere both by direct emissions such as fossil-fuel combustion or wind (primary particle production) and by gas-to-particle conversion (secondary particle production). Globally, both of these pathways are expected to be important, since secondary particle production has also been observed to take place in a number of different atmospheric environments (Clarke, 1992; Covert et al., 1992; Weber et al., 1999; Birmili and Wiedensohler, 2000; Harrison et al., 2000; O'Dowd, 2001). However, while the primary aerosol sources can be reasonably well characterized, the exact mechanisms underlying the secondary aerosol formation are far from being understood.

There are strong reasons to believe that a first step in the secondary particle formation is nucleation which produces nanometer-size thermodynamically stable clusters (e.g. Kulmala et al., 2000). Under favourable conditions, this is followed by the growth of these clusters to detectable sizes so that an apparent particle formation event can be observed. The bulk growth of freshly-nucleated clusters and subsequently formed particles in the atmosphere is mainly explained by condensation of organic vapours (Marti et al., 1997; Kavouras et al., 1998; Leaitch et al., 1999; Yu et al., 1999; Kerminen et al., 2000; Kulmala et al., 2001a), even though sulphuric acid is expected to drive particle formation under certain circumstances (Birmili et al., 2000). There are also indications that nanometer-size particles formed in the atmosphere might be organic, or that they would at least have a major organic fraction (O'Dowd et al., 2002) as well as being well soluble in water (Hämeri et al., 2001). What is lacking, however, is a detailed explanation for the formation of organic particles in the atmosphere that would account for the different physico-chemical processes involved.

In this modelling study, we investigate in detail how organic particles are formed in the atmosphere. Our main goals are to present a mechanism explaining the growth of nanometer-size clusters by condensation of organic vapours, and to identify the factors limiting the production of organic particles with a particular attention paid to the relative

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roles played by organic vapours and gaseous sulphuric acid in this process.

The paper is organized as follows. First, we introduce a recently developed theory that describes accurately the physico-chemical interactions between nanometer-size clusters with condensing organic vapours (Kulmala et al., 2003). By coupling it with a relatively simple box-model, we then investigate the implications of the theory to organic particle formation. Finally, we apply the obtained results to explaining seasonal variation in the number of aerosol formation events that has been observed during continuous measurements carried out at a continental forest site in Finland.

2. Nano-Köhler theory

It has been suggested that organic particles are formed in the atmosphere via condensation of organic vapours into freshly-nucleated inorganic clusters (e.g. Kulmala et al., 2000). In principle, organic vapours could also participate into nucleation, even though it is quite uncertain whether this can take place under real atmospheric conditions (Gao et al., 2001; Bonn et al., 2002). Here we do not explore this pathway but focus on explaining how organic particles are formed from inorganic clusters. To this end, we apply a recently developed theory which is called as a nano-Köhler theory.

2.1. Activation of atmospherically formed clusters

Here only a short description of the nano-Köhler theory is given since a detailed description of the approach was presented in our previous paper (Kulmala et al., 2003). Briefly, the nano-Köhler theory is analogous to the traditional Köhler theory the difference it describes the equilibrium of droplets consisting of liquid phase salt-water-organic species with water and organic vapour. The equilibrium for water (*wat*) and water-soluble organic vapour (*os*) are determined by the following equations (Laakso-

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nen et al., 1998):

$$S_{os} = x_{os} \times \gamma_{os} \times \exp\left(\frac{a_{os}}{d_c}\right),$$
$$S_{wat} = x_{wat} \times \gamma_{wat} \times \exp\left(\frac{a_{wat}}{d_c}\right), \quad (1)$$

where $a_i = 4\sigma v_i / RT$. Here the subscript i denotes either the organic species or water, x_i is mole fraction and γ_i the activity coefficient of i , a_i corresponds to the Kelvin term, d_c is the diameter, σ is the surface tension, R is the gas constant and T , temperature.

To solve the equilibrium equations simultaneously, the values of the activity coefficients γ_{os} and γ_{wat} as well as the surface tension need to be estimated. Doing so, we applied a simplified, yet non-ideal, thermodynamic model to the system. It was assumed, reasonably, that the multi-component system behaves as a pseudo-binary system comprising ionic salt and associated water molecules as one component and the organic species as the second component (Petersen et al., 2001). The pseudobinary activity coefficients are described using Van Laar equations, and the activity coefficient of water is obtained by multiplying the pseudobinary activity coefficient by that of water in a pure water-ammonium bisulphate solution (Tang and Munkelwitz, 1994). For surface tension, we applied equations which have been used to fit surface tensions of aqueous supercooled carboxylic acid solutions (Alvarez et al., 1997). Thus, the system contains 5 free parameters, including the size of the organic molecule. Here the value of $2.25 \times 10^{-28} \text{ m}^3$ is used. Since the actual organic species is unknown, so are its thermodynamic properties. Nevertheless, we utilised existing hygroscopic-growth data (Hämeri and Väkevä, 2000) for 10 nm particles to determine the thermodynamic properties of the organic species and consequently reduce the number of free variables. The existing data indicate that 10 nm particles comprise 20–30% ammonium bisulphate and 70–80% organic species. Using this chemical composition, and the measured hygroscopic growth factors of the aerosol (i.e. growth from dry conditions to relative humidities between 70% and 90%), we fitted the thermodynamic parameters

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to the experimental data and thereby constrained the value range of these parameters.

After the thermodynamic parameters have been fixed, equilibrium saturation ratios for the water-soluble organic vapour can be calculated by solving iteratively the above-presented equilibrium equations (Fig. 1). Analogous to the traditional Köhler theory, nucleated clusters become activated, i.e. they start growing by spontaneous condensation after S_{OS} exceeds its peak equilibrium value. A comparison of the Kelvin term with the equilibrium curves of S_{OS} shows that homogenous nucleation of the organic vapour requires supersaturations that are typically several orders of magnitude higher than those required for cluster activation via nano-Köhler mechanism, making the latter pathway much more favourable for particle formation. Furthermore, the peak equilibrium saturation ratio decreases very strongly as the size of an inorganic seed in a cluster increases: activation of clusters having initial diameters of 1.2 and 2 nm requires supersaturations around 10^3 and 10, respectively. However, the supersaturations required for cluster activation and subsequent growth exceed clearly unity in any case, arising the question “is it possible that any organic vapour reaches such high supersaturations under real atmospheric conditions?”. This question is considered in the next section.

2.2. Factors determining the saturation ratio of an organic vapour

Whether an atmospheric cluster population will become activated by a condensing organic compound and subsequently grow to larger sizes depends on how large values the saturation ratio of this organic compound, S_{OS} , will reach. This depends in turn on complex interactions between the condensing organic vapour, freshly-formed clusters and a pre-existing aerosol population. In this section, we discuss the factors affecting S_{OS} and introduce an explicit equation describing its time development.

Insight into the considered dynamics can be gained by considering the differences between the cloud droplet activation caused by the condensation of water vapour and the activation of nanometer-size particles caused by the condensation of an organic vapour as described by the nano-Köhler theory. First, the gas-phase concentration

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of water vapour is around 10^{16} – 10^{17} molecules cm^{-3} , whereas that of the condensing organic vapour is estimated to be between 10^6 – 10^8 molecules cm^{-3} (Kulmala et al., 2001b; Dal Maso et al., 2002). Second, the activating cloud droplets consume effectively the available water vapour in a cloud updraft, thereby limiting the activation process itself. As a result the saturation ratio of water vapour does not reach very large values during a cloud formation, but stays typically below 1.01 (e.g. Seinfeld and Pandis, 1998). In contrast, the loss rate of the organic vapour to aerosol particles is determined by a pre-existing particle population, not by nanometer-size clusters and secondary particles. Therefore the saturation ratios reached by the condensing organic vapour differ substantially from those of water vapour. Next, we give a quantitative formulation to this point.

The gas-phase concentration of a condensing organic vapour, C_{os} , develops in time according to the following equation:

$$\frac{dC_{os}}{dt} = Q - CS \times C_{os}. \quad (2)$$

Here Q (molecules $\text{cm}^{-3} \text{s}^{-1}$) is the production rate of the condensing organic vapour and CS (s^{-1}) is a so-called condensation sink that describes the loss rate of a condensing vapour onto the particle surfaces (see, e.g. Kulmala et al., 2001b). Because of their larger size, pre-existing particles make a dominant contribution to the value of CS rather than secondary particles. We assume here that the organic vapour condenses irreversibly into pre-existing particles, i.e. its saturation vapour pressure is equal to zero over the surfaces of these particles. In Sect. 3, the validity of this assumption will be justified.

Using Eq. (2), an equation for the time development of the saturation ratio $S_{os} = C_{os}/C_0$ easily follows:

$$\frac{dS_{os}}{dt} = \frac{Q}{C_0} - CS \times S_{os} - \frac{S_{os}}{C_0} \frac{dC_0}{dt}, \quad (3)$$

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where C_0 is the saturation vapour pressure of the organic vapour as a pure compound. If Q , C_0 and CS do not change too rapidly, S_{OS} will reach a quasi-steady state, $S_{OS,SS}$. In order to give a suitable expression to this quantity, we neglect the time dependence of the parameter C_0 (a more detailed discussion on this issue is postponed to Sect. 4.4). By doing this and setting the left-hand side of Eq. (3) equal to zero, the following equation for $S_{OS,SS}$ is obtained:

$$S_{OS,SS} = \frac{Q}{CS \times C_0} = \frac{C_{OS,SS}}{C_0}. \quad (4)$$

Here $C_{OS,SS} = Q/CS$ is the steady-state concentration of the organic vapour. From Eq. (4) it can be seen that under conditions where S_{OS} follows closely its steady state value, S_{OS} will peak when the ratio Q/CS reaches its maximum.

It is worthwhile to apply Eq. (4) in estimating whether S_{OS} may exceed the maximum equilibrium saturation ratios over the surfaces of clusters having a diameter between 1–2 nm (Sect. 2.1). First, the estimated values for Q are $\sim 10^5$ molecules $\text{cm}^{-3} \text{s}^{-1}$ during aerosol formation events taking place at a remote continental site (Kulmala et al., 2001b; Dal Maso et al., 2002). The values for CS are typically of order of 0.001s^{-1} in the same site. Finally, C_0 of the condensing organic vapour has been estimated to be $< 10^6 - 10^7$ molecules cm^{-3} (Kulmala et al., 1998; Kerminen et al., 2000; Anttila and Kerminen, 2003; Bonn and Moortgat, 2003). Inserting these values into Eq. (4), it can be seen that S_{OS} obtains values $> 10 - 100$ during aerosol formation events. By looking at Fig. 1 it can be thus concluded that the estimated value range of S_{OS} , derived from ambient data and independent modelling results, is consistent with the peak equilibrium saturation ratios produced by the nano-Köhler theory. This comparison indicates that the activation of nanometer-size clusters via nano-Köhler mechanism can take place under real atmospheric conditions, motivating a deeper study of the dynamics involved.

According to Eq. (4), pre-existing particles play a central role in the time development of S_{OS} . In addition, these particles affect crucially the number concentration of

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both newly-formed clusters and activated particles via coagulative scavenging (Kerminen et al., 2001). Therefore, when searching for the conditions under which notable aerosol formation may take place, the coagulative loss of clusters and very small particles has also to be accounted for. Because of all complex interactions involved, we have constructed a numerical model that simulates the appropriate physico-chemical processes.

3. Model description

The numerical model employed in this study couples the nano-Köhler theory with a box model simulating the time development of an atmospheric aerosol population. Nucleation and coagulation are included, as well as the production of condensing vapours and their transfer between the gas and aerosol phase. The ambient conditions are described by two parameters which are the temperature and relative humidity. While the model is in some respects highly simplified, it can still be considered detailed enough to give an overall picture on the activation dynamics of nanometer-size clusters in the atmosphere. In the following we describe how the discussed processes along with the nano-Köhler theory are implemented in the model.

3.1. Gas-phase chemistry

The modelled gas-phase chemistry includes the formation of sulphuric acid and condensing organic compound. Sulphuric acid is produced via the oxidation of SO₂ by OH radicals with a reaction rate constant equal to 1×10^{-12} molecules⁻¹ cm³. The SO₂ concentration is assumed to be temporally constant, whereas the OH radical concentration follows a diurnal cycle: $[\text{OH}] = [\text{OH}]_{\text{max}} \exp[-((t-12)/\tau_{\text{OH}})^2]$. Here t is the local time in hours, τ_{OH} describes how rapidly the OH radical concentration decreases from its maximum value, $[\text{OH}]_{\text{max}}$, which is reached at noon. For $[\text{OH}]_{\text{max}}$ and τ_{OH} , values equal to 5×10^6 molecules cm⁻³ and 3 h, respectively, were chosen.

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At present there is a considerable uncertainty concerning the pre-cursor emission rates and gas-phase reaction mechanisms that lead to the formation of organic compounds of extremely low saturation vapour pressures (Kesselmeier and Staudt, 1999; Bonn et al., 2002; Ziemann, 2002). However, we do not require exact knowledge of these mechanisms, since qualitative features related to the activation behaviour are independent of them. Therefore the production term of the organic vapour, Q , is modelled by assuming that it is tied to the gas-phase concentration of OH radical, i.e. $Q = P_{\max} \exp[-((t-12)/\tau_{\text{prod}})^2]$. The maximum production rate P_{\max} is chosen so that the overall magnitude of Q matches with estimates presented by Kulmala et al. (2001b) and Dal Maso et al. (2002).

3.2. Aerosol processes

Rather than applying the currently available nucleation theories or their parametrizations the nucleation rate, J_{nuc} , is kept here as a free parameter. This approach is sufficient for our purposes, since a more complex treatment of the nucleation process is beyond the scope of this study.

Coagulation of clusters and newly-formed particles with a pre-existing particle population, as well as their mutual coagulation is treated by taking into account Brownian coagulation only. In contrast, self coagulation of a pre-existing particle population is neglected.

The mass transfer of the organic vapour and sulphuric acid between the gas phase and particles is simulated explicitly using the expression by Fuchs and Sutugin (1971). Mass accommodation coefficients and gas-phase diffusion coefficients of both the organic vapour and sulphuric acid are assumed to be equal to unity and $0.1 \text{ cm}^2 \text{ s}^{-1}$, respectively. The condensational fluxes of these vapours are driven by the difference ($C_i - C_{i,\text{eq}}$), where C_i is the gas-phase concentration and $C_{i,\text{eq}}$ saturation vapour pressure over the particle surface. The magnitude of $C_{i,\text{eq}}$ for sulphuric acid is assumed to be negligible, i.e. it is set equal to zero. In the case of nucleation mode particles, $C_{i,\text{eq}}$ for the organic vapour is calculated according to the nano-Köhler theory. The

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saturation vapour pressure of the organic vapour as a pure compound, C_0 , is set equal to 1×10^6 molecules cm^{-3} . This value has been chosen according to estimates obtained from numerical simulations and empirical data (Kulmala et al., 1998; Kerminen et al., 2000). As pointed out when presenting Eq. (2), $C_{i,eq}$ for the organic vapour was assumed to be zero over the surfaces of pre-existing particles. The validity of this approximation was tested by conducting a few model runs in which the nano-Köhler theory was used to calculate $C_{i,eq}$ also for the pre-existing particle population. These simulations showed that the exact results differ marginally (up to a few percent) from those obtained using the approximate treatment. Finally, the gas-to-particle transfer of ambient water vapour is simulated assuming a thermodynamic equilibrium between the gas and particle phase. The particle water content is therefore given directly by the nano-Köhler theory.

3.3. Treatment of the aerosol size distribution

The pre-existing aerosol population is assumed to consist of two lognormal modes corresponding to the Aitken and accumulation mode. The particles are put into 40 equally-spaced size sections which span the diameter range $0.01\text{--}1\ \mu\text{m}$. The particle chemical composition is assumed to be uniform within each section. Under real atmospheric conditions, the particle size distribution is modified by condensation, coagulation, dilution and deposition processes. Here the size distribution of a pre-existing particle population is held fixed during a simulation, unless otherwise mentioned. The main advantage of this assumption is that the condensation sink CS in Eqs. (2)–(4) stays constant during the whole model run. This simplification, while not affecting the general behaviour of the system significantly, makes it easier to analyse the model runs and to show the most important features of the obtained results.

The time evolution of clusters and nucleation mode particles are simulated using 100 size sections. For the size distribution representation we chose a moving sectional technique because of its advantages in simulating condensation dominated problems (Zhang et al., 1999). In order to handle continuous nucleation in the moving-grid frame,

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the following approach is used: each simulation is divided into 100 time intervals corresponding to the number of size sections. After each time interval, all clusters nucleated during this time are put into a new size section, which is then allowed to move in size independent of other size sections as a result of condensation and coagulation processes. The initial number of clusters in each section is therefore the nucleation rate times the length of the time interval. Additionally, these clusters are assumed to have an initial diameter of 1 nm and to consist of ammonium bisulphate and water. As in the case of pre-existing particles, the chemical composition of the clusters and subsequently formed particles is assumed to be uniform within each size section.

4. Model simulations

The presentation of the simulation results is organized as follows. Section 4.1 is devoted to the most central features of the activation dynamics. After this, effects of a pre-existing particle population are discussed (Sect. 4.2), followed by a closer look at the influence of the nucleation rate (Sect. 4.3). Finally, the role of ambient conditions in activation dynamics is considered briefly in Sect. 4.4.

4.1. General features of activation dynamics

Figure 2 shows how the gas-phase concentrations of the condensing vapours developed in time during the investigated model runs. In all these simulations, the values of the input parameters were chosen according to conditions typical for continental background areas (Weber et al., 1997; Birmili et al., 2000; Mäkelä et al., 2000; Kulmala et al., 2001b; Dal Maso et al., 2002). As can be seen, the concentration of both sulphuric acid and organic vapour built up in the morning, reached their maximum at noon and began to decrease in the afternoon. The concentration levels produced by the model are consistent, in the case sulphuric acid, with ambient measurements (Weber et al., 1997; Birmili et al., 2000) and, in the case of the organic vapour, with indirect

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estimates based on observed particle growth (Kulmala et al., 2001b; Dal Maso et al., 2002). These concentrations were also compared with the respective steady-state values. A close agreement between these two quantities was found, which demonstrates that Eq. (4) gives a good approximation to the saturation ratio of the condensing organic vapour.

The activation behaviour of clusters is illustrated in Fig. 3, which depicts the time development of the diameter and number concentration of clusters and newly-formed particles in a few selected size sections. The first size section contains clusters formed at 08:00 local time, i.e. at the beginning of the model run. Due to the low gas-phase concentrations of the condensable gases at that time, practically all of these clusters coagulated away before reaching larger sizes. In contrast, clusters formed around 11:00 local time grew sufficiently fast to overcome complete coagulative scavenging, such that a fraction of them survived throughout the simulation. The cluster growth rate was considerably enhanced after they reached sizes of around 2 nm in diameter. Below this size range, the organic vapour was not supersaturated with respect to the clusters and the condensational growth was driven by sulphuric acid alone. After reaching the threshold size, the clusters became activated with respect to the organic vapour which led to a rapid growth of the clusters and suppression of their coagulative scavenging. The growth slowed down in the afternoon as the gas-phase concentrations of the condensing vapours started to decrease. As a result, clusters formed in the evening or late afternoon experienced the same fate as those formed in the early morning, i.e. they were rapidly scavenged away by larger particles.

Figure 4 shows the size distribution of nucleated clusters and subsequently formed particles in the same model run at different local times. The first size distribution is at 3 h from the start of the simulation, i.e. at 11:00 local time. At this stage some of the clusters have already activated and consequently grown to detectable sizes. One hour, a distinguishable nucleation mode has been formed and the largest newly-formed particles have reached sizes of around 10 nm in diameter. Assuming that these particles were nucleated in the beginning of the simulation, it can be inferred that their growth

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rate was around 2 nm/h. This estimate is consistent with observed particle growth rates in remote continental sites (e.g. Birmili et al., 2000; Mäkelä et al., 2000). The particle formation and growth continued for a few hours after the midday, but eventually the gas-phase concentrations of the condensing vapours decreased to such low levels that they could not sustain any significant growth. Along with rapid coagulation scavenging this led to a shortage of clusters and particles in the size range 1–5 nm. As seen from the third size distribution, the formation of the resulting “gap” begins in the afternoon and is clearly seen in the last size distribution which is at the evening (20:00).

Further insight into the activation dynamics can be gained from Fig. 5, which shows the time evolution of the total number concentration and mean diameter of newly-formed particles. The importance of sulphuric acid in the particle formation is evident. When the gas-phase concentration of sulphuric acid stayed $<3 \times 10^6$ molecules cm^{-3} (see Fig. 2), the clusters were scavenged by larger particles before they could activate. Consequently, notable particle formation did not take place in these simulations. When the maximum concentration of sulphuric acid was $>5 \times 10^6$ molecules cm^{-3} and P_{max} had values around 10^5 molecules $\text{cm}^{-3} \text{s}^{-1}$, freshly-nucleated clusters grew rapidly to sizes of around 2 nm, after which they became activated with respect to the organic vapour. In these cases, the appearance of particles having a diameter >3 nm can be seen after 2–4 h from the start of a simulation, i.e. between 10:00 and 12:00 local time. The number concentration of formed particles rose rapidly until the early afternoon, after which the particle concentration started to decrease due to coagulation. The mean diameter of the newly-formed particles increased until the late afternoon when it reached values between 10 and 20 nm. After this, the particle growth slowed down due to the low gas-phase concentrations of the condensing vapours.

Sulphuric acid was not able to induce a significant particle formation by itself unless its maximum gas-phase concentration was $>10^7$ molecules cm^{-3} . This was seen by conducting model runs in which the production rate of the organic vapour was set equal to zero. In these simulations, the gas-phase concentration of sulphuric acid had to reach values of around 5×10^7 molecules cm^{-3} before particles having a diam-

eter >10 nm were formed in noticeable amounts. Otherwise a clear majority of newly-formed particles remained in the size range <10 nm.

4.2. Effects of a pre-existing particle population

Pre-existing particles affect the activation dynamics in two ways: they act as a sink for condensable vapours (Eq. 4) and reduce the number of clusters and newly-formed particles via coagulative scavenging. The parameter CS provides a suitable measure for both of these effects and therefore we investigated more closely this issue by performing a set of model runs in which the value of CS was varied (Table 1).

An apparent feature seen from the simulation results is that the particle formation is reduced with an increase in the value of CS . This effect is compensated to a some extent by an enhanced production of sulphuric acid and organic vapour. However, even if the production terms of condensing vapours are increased in such a way that their gas-phase concentrations stay about the same, the number of nucleation mode particles decreases as the value of CS is increased because freshly-formed clusters are scavenged away more rapidly. On the other hand, if the production terms do not increase in pace with CS , the gas-phase concentrations of condensing vapours might decrease to such an extent that the particle formation is completely suppressed.

4.3. Cluster growth by self coagulation

The model runs presented in Sect. 4.1 demonstrated that freshly-nucleated clusters have to reach a diameter of around 2 nm before they can activate with respect to organic vapours. In addition, it was concluded that sulphuric acid is able to grow clusters effectively into this threshold size at concentrations typical for continental background areas. Another mechanism which makes nucleated clusters grow is their self coagulation. If the number of clusters is sufficiently high, this mechanism might therefore provide another pathway for an initial cluster growth. We addressed this issue by conducting a number of simulations in which the value of the nucleation rate, J_{nuc} , was

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varied (Table 2).

From Table 2 it can be seen that the magnitude of the parameter J_{nucl} must be order of $10^3 \text{ cm}^{-3} \text{ s}^{-1}$ or greater to make clusters grow by coagulation so rapidly that a significant particle formation results. The effectiveness of self coagulation in growing clusters depends strongly on a pre-existing particle population. For example, the value of J_{nucl} had to be increased from $\sim 10^3$ to $\sim 5 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ as the value of CS was increased from 2×10^{-3} to $4 \times 10^{-3} \text{ s}^{-1}$ to sustain a notable particle formation.

In order to find out whether self coagulation has importance to cluster growth under real atmospheric conditions, we compared these values of J_{nucl} with the estimated cluster formation rates in a continental background site (Kulmala et al., 2001b; Dal Maso et al., 2002). These studies indicate that stable clusters having a diameter 1 nm are formed at rates ranging from 10 to $10^2 \text{ cm}^{-3} \text{ s}^{-1}$. Accordingly, self coagulation is expected to be of secondary importance when considering the initial stages of cluster growth in continental background areas. It should be noted, however, that this conclusion does not necessarily hold in a case of e.g. coastal environment, where the estimated cluster formation rates may exceed those in continental background areas by several orders of magnitude (O'Dowd et al., 1998). Furthermore, cluster growth driven by self-coagulation leads to a considerable reduction of their number concentration. For example, if clusters grow from 1 to 3 nm in diameter via self-coagulation, their number concentration is reduced by a factor of 27.

4.4. Effects of ambient conditions

In the model runs presented so far, the parameters describing ambient conditions, namely the temperature (T) and relative humidity (RH), were held constant. Furthermore, the influences of meteorological processes on the concentration levels of particles and condensing vapours were not accounted for, even though all these quantities exhibit both temporal and spatial variation due to changes in atmospheric conditions. The effects of these variations on particle formation cannot be fully explored, since

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our current understanding concerning several key processes, such as the exact gas-phase chemistry involved and nucleation, is far from complete. Here we focus on those effects that can be quantified using the developed numerical model and simple theoretical considerations. In particular, we do not investigate whether fluctuations in the concentrations of condensing vapours are able to enhance cluster activation (in a case of cloud droplet activation this has been suggested to occur, see Kulmala et al., 1997).

Changes in temperature affect primarily the saturation ratio of the organic vapour, S_{os} , due to the exponential temperature dependence of the vapour pressure. Since particle formation typically begins in the morning, it is worthwhile to consider whether the temperature changes at that time of day could affect the time development of S_{os} . In order to estimate the importance of this effect, we apply the Clausius-Clapeyron equation in Eq. (3) and obtain:

$$\frac{dS_{os}}{dt} = \frac{Q}{C_0} - S_{os} \times \left(CS + \frac{\Delta H_{os}}{R \times T^2} \times \frac{dT}{dt} \right). \quad (5)$$

Here ΔH_{os} (J mol^{-1}) is the enthalpy of vaporization and R is the ideal gas constant. The last term in parenthesis in the right-hand side of (8) contains the temperature dependence of S_{os} . The relative importance of this term can be estimated by comparing its magnitude with that of CS . The enthalpies of vaporization for atmospheric organic compounds are typically $<170 \text{ kJ mol}^{-1}$ (Strader et al., 1999; Sheehan and Bowman, 2002) and the temperature changes probably no faster than a few Kelvin degrees per hour. The value of the considered term is thus $<10^{-4} \text{ s}^{-1}$ in the temperature range $>273 \text{ K}$. Since the value of CS is $>10^3 \text{ s}^{-1}$ in continental boundary layers, it can be concluded that diurnal variation of the temperature has only a minor effect on the time development of S_{os} and, consequently, to particle formation taking place at continental areas.

An air parcel where the particle formation takes place may experience convective updrafts that cause a rapid cooling of the parcel. The influence of this process to the time development of S_{os} can be estimated using Eq. (5). In the case of adiabatic cool-

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ing, the maximum temperature change is given by the dry adiabatic lapse rate which is equal to -9.8 K km^{-1} (e.g. Seinfeld and Pandis, 1998). Assuming further that the vaporization enthalpy of the organic vapour and updraft velocity are equal to 170 J mol^{-1} and 1 m s^{-1} (which are upper limit estimates for these parameters) respectively, a value of around 10^{-3} s^{-1} for the last term in the parenthesis in the right hand side of (8) is obtained. This value is of the same magnitude than that of CS . Therefore, under extreme conditions, the effect of adiabatic cooling to the time development of S_{OS} may be comparable to that of the condensational loss, demonstrating the potential importance of meteorological processes to the activation behaviour.

In the developed model relative humidity affects primarily the water uptake of clusters and particles. Since a pre-existing particle population tends to absorb more water at higher relative humidities, it becomes a larger sink for condensing vapours, newly-formed particles and clusters as RH increases. Correspondingly, the value of CS is reduced with a decrease in RH . Using the numerical model, it was calculated that the value of CS may change up to a factor of two as RH varies in the range 60–90%. Chemical composition of freshly-formed clusters depends also on RH such that their activation is favoured at higher relative humidities. However, model runs in which relative humidity was varied indicated that this effect is dominated by the variation of CS with RH .

Finally, we investigated how the diurnal behaviour of an atmospheric mixed layer influences particle formation taking place within. The considered time of day is the morning, during which the height of the mixed layer grew rapidly as a response to the solar heating. The associated dilution of air within the mixed layer resulted in a decrease in the number concentration of pre-existing particles, thereby favouring formation of new particles. The growth of the mixed layer height was modelled by forcing the value of CS along with the concentrations of clusters and newly-formed particles to decrease linearly a few hours starting at 09:00 local time. The duration and magnitude of the decrease were chosen according to Nilsson et al. (2001) and Dal Maso et al. (2002). Performed model runs demonstrated that the mixed layer

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growth may reduce the pre-existing particle concentrations such that apparent particle formation results. For example, during a model run in which the value of CS decreased from $4 \times 10^{-3} \text{ s}^{-1}$ to around $2.5 \times 10^{-3} \text{ s}^{-1}$ in 3 h, the number of newly-formed particles reached values of around $1.2 \times 10^3 \text{ cm}^{-3}$. In contrast, no particle formation did take place when the value of CS was kept equal to $4 \times 10^{-3} \text{ s}^{-1}$ throughout the model run.

5. Seasonal variation of aerosol formation events

Organic vapours that may become sufficiently supersaturated to cause the activation of clusters nucleated in the atmosphere have probably a very low vapour pressure, i.e. $< 10^6 - 10^7 \text{ molecules cm}^{-3}$ (Kulmala et al., 1998; Kerminen et al., 2000; Anttila and Kerminen, 2003). Although there has been some progress in understanding the chemical mechanisms that might produce such compounds in the atmosphere (Tobias and Ziemann, 2000; Tobias et al., 2000; Bonn et al., 2002; Ziemann, 2002), their identity and exact physico-chemical properties remain still unclear. This is one of the major reasons why the developed theory cannot be properly tested against experimental data. However, the following illustrates that the results obtained in this study are consistent with many features related to aerosol formation events taking place at continental areas.

A five-year-long data set on observed particle formation events at a continental forest site in Finland displays a strong seasonal variation in the number of occurrence of these events, with a maximum during the spring and a minimum in summer (Kulmala et al., 2001a). The processes investigated in the present paper (formation of inorganic clusters by nucleation, their initial growth by sulphuric acid, and their activation by organic vapours) can explain this feature. Using the measured UV radiation and SO_2 concentration data, as well as data on calculated condensation sinks, the estimated sulphuric acid concentration at the site is on average 3 times higher in spring than in summer. At the same time, the average saturation vapour pressure of organic vapours (estimated using observed temperature data and a typical temperature dependence of C_0 for organic vapours) is roughly a factor 4 smaller in spring than in summer. Thus, in

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the springtime the inorganic clusters are expected to grow approximately 3 times more rapidly than in summer before their activation, in addition to which the needed organic vapour concentration for activation is clearly smaller in spring. Together, these things explain the basic physics behind why we have more particle formation events in spring than in summer. The observed growth rates of newly-formed particles are 3–4 times higher in summer than in spring. This is also consistent with our results, because at summertime the growth rates should be significantly higher due to the higher organic vapour concentrations needed to reach a certain value of S_{os} .

6. Summary and conclusions

We have applied a recently-developed theory, called the nano-Köhler theory, to explain how organic particles are formed from freshly-nucleated inorganic clusters. The nano-Köhler theory, being analogous to the traditional Köhler theory, implies that after reaching a certain threshold size, nucleated clusters are activated, i.e. they start growing by spontaneous condensation of a water-soluble organic vapour. In order to investigate under which conditions this might result in a considerable particle formation, the nano-Köhler theory was coupled with a box-model simulating the appropriate aerosol and gas-phase processes. The model was able to reproduce qualitative features related to particle formation events taking place at background continental areas and provided a novel insight into this phenomenon.

The performed simulations indicated that the growth of freshly-nucleated clusters and subsequently formed organic particles is driven both by gaseous sulphuric acid and organic vapours. Sulphuric acid is responsible for the initial growth of the clusters to sizes around 2 nm in diameter. After the clusters have reached this threshold size, they become activated by an organic vapour. Under favourable conditions, this is followed by a rapid growth of the clusters so that a distinguishable particle formation event takes place.

In the absence of sufficient amounts of gaseous sulphuric acid, self coagulation of

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clusters may provide an alternative pathway for their initial growth. The conducted simulations revealed that this mechanism is effective only when thermodynamically stable clusters are formed at rates $>10^3$ molecules $\text{cm}^{-3} \text{s}^{-1}$. Whether such high nucleation rates take place at continental boundary layers cannot be conclusively assessed at present. However, indirect evidence obtained from a remote continental site indicates that the actual nucleation rates might be lower than this value by an order of magnitude or more (Kulmala et al., 2001b; Dal Maso et al., 2002), implying that condensation of sulphuric acid is a more viable mechanism for the initial growth of nucleated clusters than their mutual coagulation.

The model runs demonstrated that a shortage of either gaseous sulphuric acid or condensing organic vapours limits, or even suppresses altogether, the organic particle formation. In a case where sulphuric acid has a sufficiently low gas-phase concentration, i.e. below the order of 10^6 molecules cm^{-3} , nucleated clusters do not reach sizes in which they are able to activate but are rapidly removed from the atmosphere by coagulative scavenging. On the other hand, gas-phase concentrations of the order of 10^7 molecules cm^{-3} are required in order that organic vapours grow nanometer-size clusters and particles effectively into nucleation mode sizes.

The conducted simulations along with theoretical considerations revealed also that meteorological processes such as dilution and adiabatic cooling of the air masses may influence the cluster activation considerably. The former process decreases the surface area of a pre-existing particle population, whereas the latter process decreases the saturation vapour pressure of the organic compound. Both of these processes lead therefore to the increase of the saturation ratio of the organic compound, alleviating the cluster activation.

Since organic vapours responsible for particle formation in the atmosphere remain to be identified, their exact physico-chemical properties are largely unknown. Because of this, we had to apply indirect experimental data when modelling the interactions between a condensing organic vapour and nanometer-size clusters. Due to the robustness of the applied framework, however, the associated uncertainties do not affect the

overall picture on organic particle formation that the present study provides. As relevant experimental data is obtained more, it can be utilized to improve the accuracy of the developed approach. Additionally, numerical models incorporating the nano-Köhler theory can be extended in future to account for processes that are not covered by the model applied here.

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Table 1. Maximum gas-phase concentrations of sulphuric acid and the organic vapour, $[H_2SO_4]$ (max) and C_{os} (max), respectively, during the 12 h simulations. The maximum number concentration of formed particles, N_{nuc} (max), and their maximum mean diameter, d_{nuc} (max), are also shown. The value range of CS are chosen according to the conditions that are typical to continental background areas (Kulmala et al., 2001b; Dal Maso et al., 2002). The values of the other input parameters were chosen as in Fig. 2.

| P_{max} , $\times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ | $[SO_2]$, ppt | $[H_2SO_4]$ (max), $\times 10^6 \text{ cm}^{-3}$ | C_{os} (max), $\times 10^7 \text{ cm}^{-3}$ | N_{nuc} (max), cm^{-3} | d_{nuc} (max), nm |
|---|-------------------|---|--|--------------------------------------|------------------------|
| $CS=2 \times 10^{-3} \text{ s}^{-1}$ | | | | | |
| 1.2 | 150 | 9.5 | 6.0 | 2400 | 19 |
| 2.5 | 150 | 9.4 | 12 | 4200 | 37 |
| 2.5 | 300 | 17 | 11 | 12 000 | 43 |
| 3.75 | 450 | 22 | 15 | 15 000 | 58 |
| $CS=4 \times 10^{-3} \text{ s}^{-1}$ | | | | | |
| 1.2 | 450 | 14 | 3.0 | 220 | 13 |
| 2.5 | 300 | 9.5 | 6.2 | 63 | 18 |
| 2.5 | 450 | 14 | 6.2 | 580 | 22 |
| 3.75 | 150 | 4.8 | 9.4 | 0 | – |
| 3.75 | 450 | 14 | 9.3 | 1000 | 31 |
| 5.0 | 600 | 19 | 12 | 3300 | 45 |
| $CS=6 \times 10^{-3} \text{ s}^{-1}$ | | | | | |
| 2.5 | 300 | 6.4 | 4.2 | 0 | – |
| 2.5 | 600 | 13 | 4.2 | 9 | 15 |
| 3.75 | 450 | 9.5 | 6.2 | 2 | 15 |
| 5.0 | 150 | 3.2 | 8.3 | 0 | – |
| 5.0 | 600 | 13 | 8.3 | 38 | 26 |

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Table 2. The maximum number concentration of formed particles, N_{nuc} (max), and their maximum mean diameter, d_{nuc} (max), during the 12 h simulations. No gaseous sulphuric acid were assumed to be present. The values of the other input parameters were chosen as in Fig. 2.

| J_{nuc} , $\text{cm}^{-3} \text{s}^{-1}$ | P_{max} , $\times 10^5 \text{cm}^{-3} \text{s}^{-1}$ | N_{nuc} (max), cm^{-3} | d_{nuc} (max), nm |
|---|---|--------------------------------------|------------------------|
| $CS=2 \times 10^{-3} \text{s}^{-1}$ | | | |
| 500 | 0.8 | 6 | 9 |
| 750 | 0.8 | 2.4×10^3 | 12 |
| 10^3 | 0.8 | 1.2×10^4 | 15 |
| 100 | 1.2 | 0 | – |
| 500 | 1.2 | 250 | 15 |
| 10^3 | 1.2 | 1.8×10^5 | 23 |
| $CS=4 \times 10^{-3} \text{s}^{-1}$ | | | |
| 2.5×10^3 | 2.5 | 4.4×10^3 | 24 |
| 5×10^3 | 2.5 | 5.7×10^4 | 34 |
| 10^4 | 2.5 | 1.7×10^5 | 43 |
| 10^3 | 3.75 | 1 | 4 |
| 2.5×10^3 | 3.75 | 8.9×10^3 | 36 |
| 5×10^3 | 3.75 | 7.0×10^4 | 44 |
| 10^4 | 3.75 | 1.5×10^6 | 88 |

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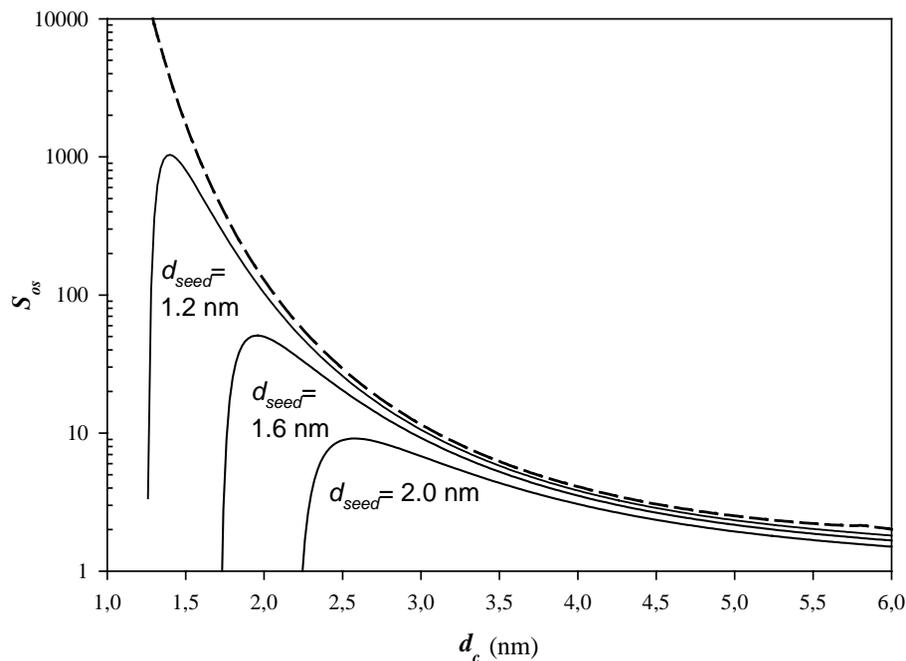


Fig. 1. The equilibrium saturation ratio of a water-soluble organic vapour above a cluster with an inorganic core of the diameter d_{seed} as a function of the cluster diameter d_c . A respective Kelvin term curve is also shown (dashed line). The ambient temperature and relative humidity were assumed to be equal to 288 K and 80%, respectively.

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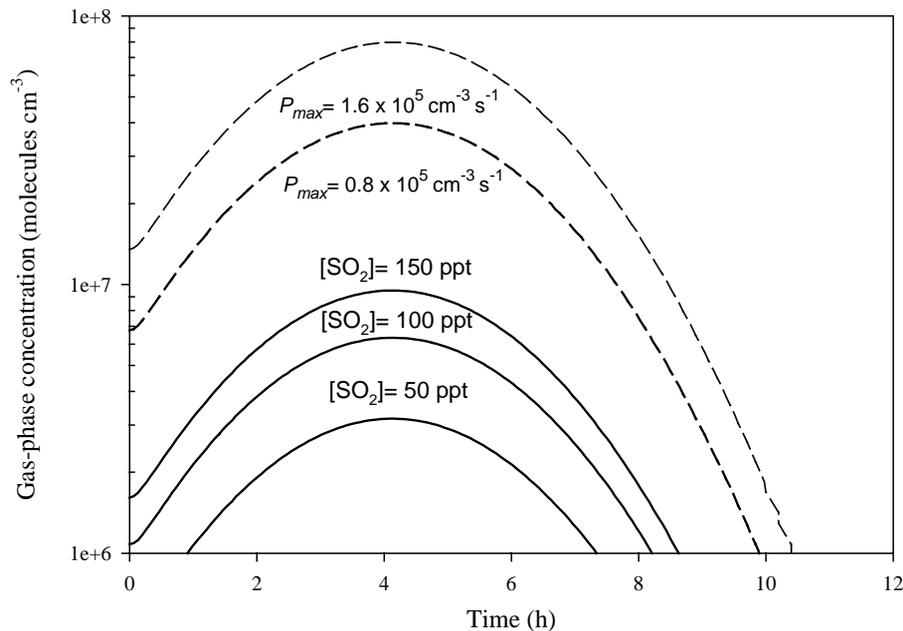


Fig. 2. Gas-phase concentration of sulphuric acid (solid lines) and the organic vapour (dashed lines) as a function of time. The simulations start at 08:00 local time and end at 20:00 local time. The parameters τ_{prod} , CS and J_{nuc} were set equal to 3 h, $2 \times 10^{-3} \text{ s}^{-1}$ and $10 \text{ cm}^{-3} \text{ s}^{-1}$, respectively. The ambient temperature and relative humidity were assumed to be equal to 288 K and 80%, respectively.

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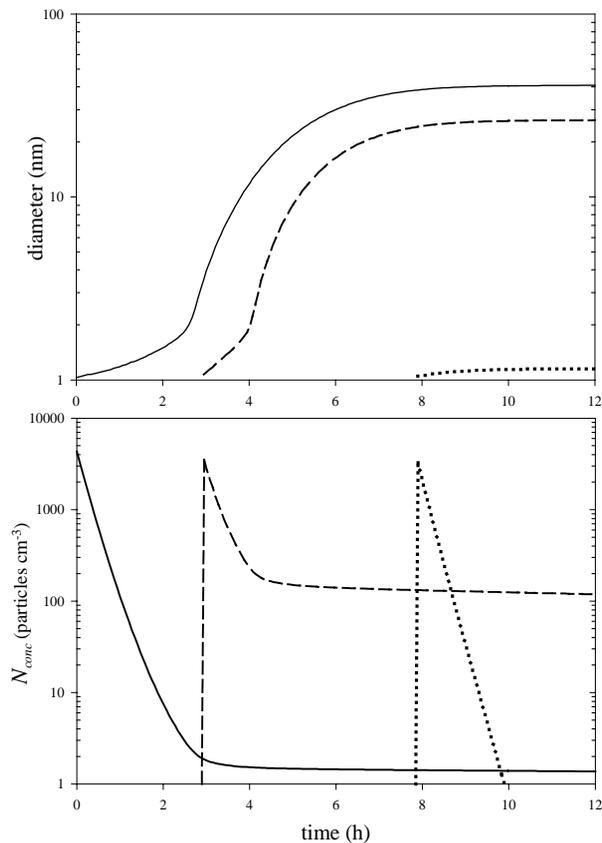


Fig. 3. The time evolution of the diameter (top) and number concentration (bottom) of clusters and newly-formed particles that are nucleated at the beginning of the simulation, i.e. 08:00 local time (solid lines), around 11:00 local time (dashed lines) and around 16:00 local time (dotted lines). The parameters P_{max} and $[\text{SO}_2]$ were chosen to be equal to $1.6 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ and 150 ppt, respectively. The values of the other input parameters were chosen as in Fig. 2.

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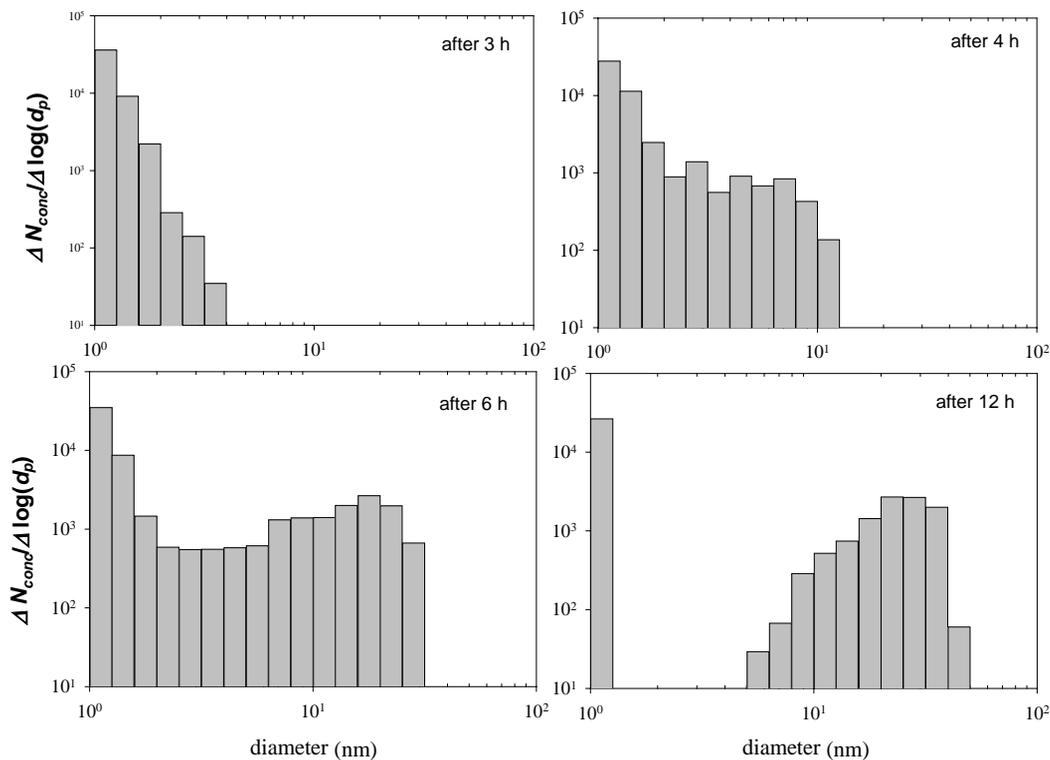


Fig. 4. The size distribution of nucleated clusters and newly-particles in the same model run at four local times. The values of the input parameters were chosen as in Fig. 3. The figures were obtained by distributing newly-formed clusters and particles into twenty size classes.

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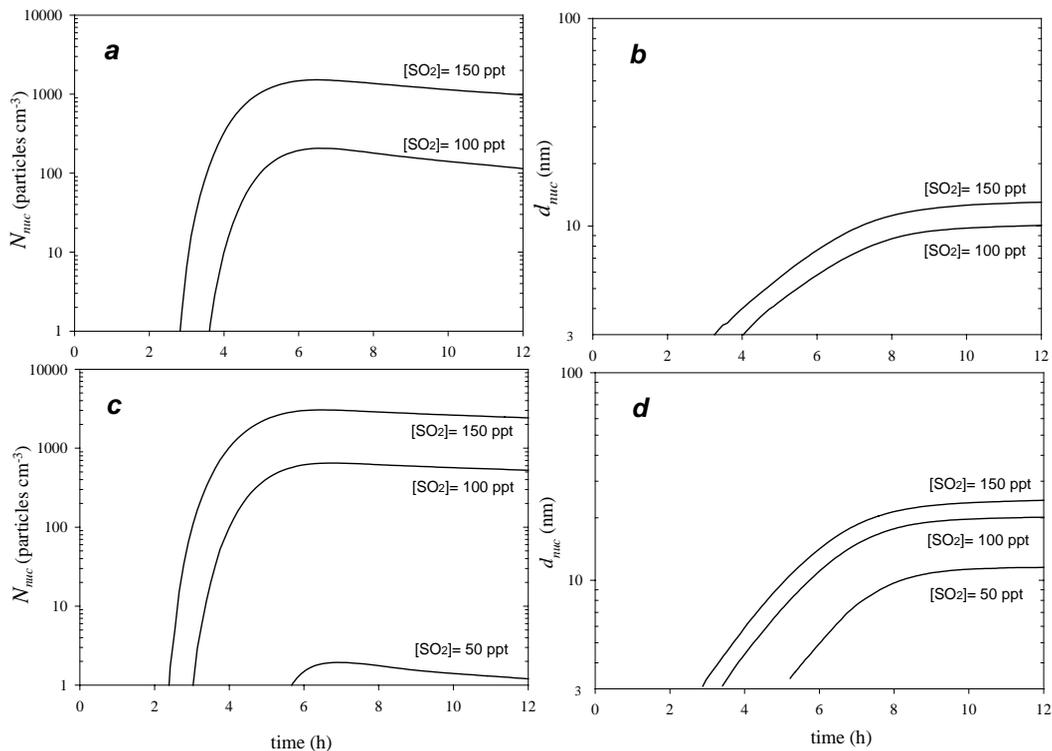


Fig. 5. Time evolution of the number concentration of detectable (>3 nm) secondary particles N_{nuc} ((a) and (c)) and the mean diameter of the particles d_{nuc} ((b) and (d)). The parameter P_{max} was set equal to $1.6 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ (top) and $8 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ (bottom). The values of the other input parameters were chosen as in Fig. 3.

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