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### Permalink

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### Journal

Atmospheric Research, 90(2-4)

### ISSN

0169-8095

### Authors

Boy, M  
Kazil, J  
Lovejoy, ER  
[et al.](#)

### Publication Date

2008-11-01

### DOI

10.1016/j.atmosres.2008.01.002

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Peer reviewed

# Relevance of ion-induced nucleation of sulfuric acid and water in the lower troposphere over the boreal forest at northern latitudes

M. Boy<sup>a,\*</sup>, J. Kazil<sup>b</sup>, E.R. Lovejoy<sup>c</sup>, A. Guenther<sup>d</sup>, M. Kulmala<sup>a</sup>

<sup>a</sup> *Division of Atmospheric Sciences, Department of Physical Sciences, P.O. Box 64, FIN-00014 University of Helsinki, Finland*

<sup>b</sup> *CIRES, University of Colorado at Boulder, CO 80309, USA*

<sup>c</sup> *NOAA Earth System Research Laboratory, Boulder, CO 80305, USA*

<sup>d</sup> *ACD, NCAR, P.O. Box 3000 Boulder, CO 80307, USA*

Received 17 September 2007; received in revised form 17 December 2007; accepted 6 January 2008

## Abstract

The relevance of ion-induced nucleation of sulfuric acid and water (IINSW) in the troposphere over the boreal forest at northern latitudes is investigated by combining two existing and previously published models (MALTE — model to predict new aerosol formation in the lower troposphere; PARNUC — a parameterized steady-state model of neutral and ion-induced nucleation of sulfuric acid and water for atmospheric conditions). Simulations were performed for 4 days with observed new particle formation at ground level by using input data from the SMEAR II station in Hyytiälä, Finland. The selected days were chosen to cover a wide range of values of the parameters most relevant for IINSW. The results showed that ion-induced nucleation of sulfuric acid and water can contribute up to 15% to the total amount of newly formed particles in the size range of 3–10 nm inside the mixed layer at the Hyytiälä site. The importance of IINSW seemed to increase in the free troposphere above the boundary layer, however, lack of measurements in the vertical structure of the input parameters suggest that the model results are burdened with high uncertainties. © 2008 Elsevier B.V. All rights reserved.

*Keywords:* Ion-induced nucleation of sulfuric acid and water; Tropospheric aerosol; New particle formation

## 1. Introduction

The role of atmospheric aerosols is, as reported in the newest report by the Intergovernmental Panel on Climate Change, still the forcing with the lowest level of scientific understanding (IPCC, 2007). Atmospheric aerosols contribute to the global radiation budget through scattering and absorption of solar radiation (direct effect) and indirectly via haze and cloud layers (Lohmann and Feichter, 2005). Aerosol number con-

centrations are strongly influenced by new particle formation from the gas phase, and both the qualitative and quantitative understanding of aerosol nucleation processes is far from complete. New particle formation has been observed at almost all sites where both particle number concentrations and size distributions have been measured; a comprehensive summary of these studies is given in Kulmala et al. (2004).

Although many field campaigns, laboratory experiments and new modeling approaches have led to a better understanding of new particle formation, its detailed mechanisms in the troposphere and their influence on environment and climate have still not been completely elucidated. We have combined two existing models —

\* Corresponding author. Tel.: +358 404 155116; fax: +358 9 19150860.

E-mail address: Michael.boy@helsinki.fi (M. Boy).

MALTE (model to predict new aerosol formation in the lower troposphere – Boy et al., 2006) and PARNUC (a parameterized steady-state model of neutral and ion-induced nucleation of sulfuric acid and water for atmospheric conditions – Kazil and Lovejoy, 2007) – to investigate the relevance of ion-induced nucleation of sulfuric acid and water in the lower troposphere over the boreal forest in Northern Europe. In this work we selected four days with observed new particle formation at the forest field station SMEAR II in Hyytiälä to investigate the contribution of IINSW to the number of newly formed particles.

## 2. Model description

### 2.1. Malte

MALTE is a one-dimensional model which includes several modules for the simulation of boundary layer dynamics and both chemical and aerosol dynamical processes. For the description of Planetary Boundary Layer (PBL) processes, a first-order closure technique is applied. The aerosol dynamics are solved by the size-segregated aerosol model, UHMA (University of Helsinki Multicomponent Aerosol model – Korhonen et al., 2004). The formation of new aerosol in the UHMA code was calculated by two different nucleation mechanisms. The first mechanism, called kinetic nucleation, is described by Kulmala et al. (2006), via

$$J = K \times [H_2SO_4]^2 \quad (1)$$

with  $K$ -coefficients in the range  $2\text{--}10 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , depending on conditions. In kinetic nucleation, critical clusters are formed by collisions of sulfuric acid molecules or other molecules containing sulfuric acid, e.g. ammonium bisulphate or organic sulfate molecules. The upper limit for kinetic nucleation, the so called “kinetic limit”, is set by the collision rate of molecules given by the kinetic theory of gases.

The second mechanism, referred to as activation type nucleation, was first proposed by Kulmala et al. (2006). In this approach, nucleation is assumed to occur due to the activation of small molecular clusters containing one sulfuric acid molecule, e.g. via heterogeneous nucleation or heterogeneous chemical reactions. Because critical clusters are assumed to contain one sulfuric acid molecule, nucleation rate is directly proportional to sulfuric acid concentration:

$$J = A[H_2SO_4] \quad (2)$$

The  $A$ -coefficients, depending on conditions, range from  $4.5\text{--}11 \times 10^{-6} \text{ s}^{-1}$ . Both coefficients ( $A$  and  $K$ , see

Table 1

Empirical predicted  $A$  and  $K$ -factors from Eqs. (1) and (2) for the selected days

| Date       | $A$ -factor [ $10^{-6} \text{ s}^{-1}$ ] | $K$ -factor [ $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ] |
|------------|--|--|
| 28.02.2006 | 4.5                                      | 0.3  |
| 03.03.2006 | 11.0                                     | 1.0  |
| 28.03.2006 | 4.5                                      | 0.2  |
| 03.05.2006 | 4.5                                      | 0.3  |

Table 1 for the detailed values) are in good agreement with earlier published values for the same site (Sihto et al., 2006; Riipinen et al., 2007).

The model meteorological variables were initialized with soundings from Jokioinen, a monitoring station of the Finnish Meteorological Institute located about 100 km south-west of Hyytiälä. The initial gas concentrations of most species – especially the organic reaction products – were set to zero during the night at the start of the model run. For several other gases such as NO, NO<sub>x</sub> and SO<sub>2</sub> we used ground measurements from the SMEAR II station (see Kulmala et al., 2001 and [www.honeybee.helsinki.fi/smea/](http://www.honeybee.helsinki.fi/smea/)) with a vertical gradient of

$$\frac{dQ(z)}{dz} = Q(z) \left( 1 - \frac{z}{16,000} \right). \quad (3)$$

The ozone mixing ratio is held constant throughout the troposphere based on SMEAR II surface measurements. These trace gas concentrations are important input parameters for the gas-phase chemistry in MALTE; their vertical gradients are based on first order approximations of simulations using the ECHAM 5 model (Risto Makkonen, personal communication).

The emissions of monoterpenes from the canopy were calculated with MEGAN (Model of Emissions of Gases and Aerosols from Nature), which is described in detail by Guenther et al., 2006. This model was implemented in MALTE and estimates landscape average emission factors for a specific location by combining estimates of plant species composition and representative species-specific emission factors. Hourly variations in estimated emissions are driven by changes in calculated leaf temperature and incident solar radiation on sun and shade leaves at different canopy levels.

The initial (midnight) aerosol concentrations and size distributions in the mixed layer are based on surface DMPS (Differential Mobility Particle Sizer) and APS (Aerodynamic Particle Sizer) measurements from the SMEAR II station. At higher altitudes, the aerosol concentrations are reduced by 50%, in consistence with

new measurements for the SMEAR II side paper under preparation.

There is currently a considerable lack of knowledge concerning the atmospheric oxidation of complex organic molecules such as monoterpenes. The identities of the end-products, their reaction yields and their physical and chemical properties are not well-characterised. Therefore, in MALTE we have assumed a yield from monoterpene oxidation of 0.05 for all reaction products capable of condensing onto nano-sized inorganic clusters and a yield of 0.05 for all products capable of being involved in a condensation mechanism depending on the properties of the vapour, the particle composition, and the shape of the particle distribution. A detailed description of the model MALTE including a discussion why we used a value of 5% for the condensation of organic vapours is given by Boy et al. (2006).

## 2.2. Parnuc

PARNUC is a model of neutral and ion-induced nucleation of sulfuric acid and water, which implements the method for calculating sulfate aerosol formation rates of Kazil and Lovejoy (2007). It calculates the steady-state formation rate of supercritical sulfuric acid/water clusters for given ambient conditions (tempera-

ture, pressure, RH, gas phase sulfuric acid concentration, ionization rate) and preexisting aerosol properties ( $\text{H}_2\text{SO}_4$  condensational sink, particle mass and diameter). Laboratory thermodynamic data for sulfuric acid uptake and loss by small neutral (Hanson and Lovejoy, 2006) and negative (Froyd and Lovejoy, 2003) sulfuric acid/water clusters are used in PARNUC, allowing for a reliable description of both the neutral and charged nucleation channel. Ion induced nucleation involving positive ions or molecules other than sulfuric acid and water, such as ammonia, is not accounted for. MALTE provides PARNUC with input data at each time step and grid point, and places the newly formed supercritical sulfate aerosol in a UHMA bin according to their size.

Ionization rates near the surface are set to  $5 \text{ cm}^{-3} \text{ s}^{-1}$  based on the measurements by Laakso et al. (2004) and Hirsikko et al. (2007) in Hyytiälä. This value included both the ionization due to radioactive decay of Radon and due to galactic cosmic rays. At higher altitudes, monthly mean galactic cosmic ray ionization rates are used. These ionization rates were obtained by interpolating the solar maximum and minimum ionization rate profiles for the location of Hyytiälä, calculated with the code of O'Brien (2005), with monthly mean Moscow neutron monitor count rates as proxy for solar activity variations.

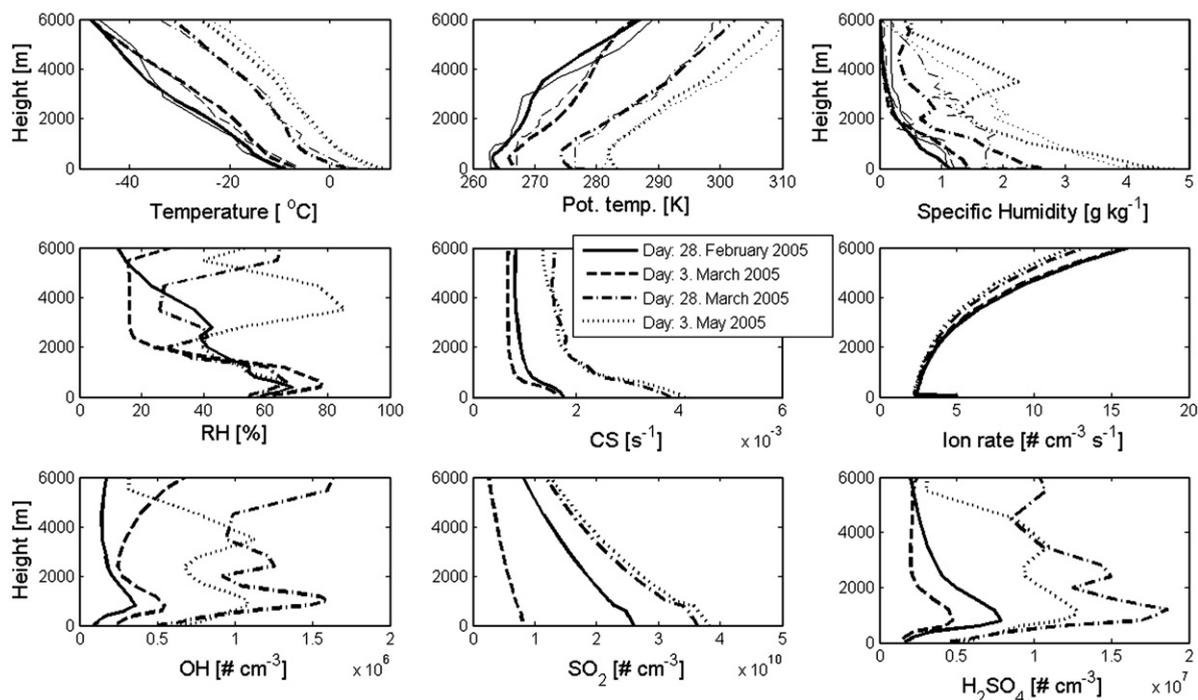


Fig. 1. Vertical profiles calculated by MALTE for the SMEAR II station in Hyytiälä for four selected days at noon (thick lines) and for temperature, potential temperature and specific humidity measured profiles from soundings at noon in Jokioinen (thin lines).

### 3. Days selected

For our model simulations we chose four days in winter and early spring 2005 with new particle formation events observed at ground level by a DMPS system. One important consideration in the selection of these days was their coverage of a wide range of values of the parameters most relevant for ion-induced nucleation. These parameters are temperature, relative humidity, preexisting aerosol  $\text{H}_2\text{SO}_4$  condensation sink (CS), and concentration of gas phase sulfuric acid. Ground level temperatures ranged from  $-15$  to  $+3$  °C at midnight on the four days. The lowest temperature, measured on the 28th of February also represents the coldest day in the year 2005 with observed new particle formation. Relative humidity reached values between 50 and 80% in the mixed layer and decreased continuously with height in the free troposphere by half on all days except for the 3rd of May. The  $\text{H}_2\text{SO}_4$  condensational sink (CS), calculated from the aerosol size distribution and temperature, gives the number of sulfuric acid molecules condensing on existing aerosols per second, and presents a first order rate coefficient for the degree of pollution in a given air mass. On the first two days – February and early March – the CS values did not exceed  $0.002 \text{ s}^{-1}$ ; indicating a less polluted air mass (see Boy et al., 2003). The following two days

( $\text{CS} > 0.004 \text{ s}^{-1}$ ) show higher aerosol background concentrations. The last parameter for ion-induced nucleation calculated by MALTE as an input-value for PARNUC is the concentration of gas phase sulfuric acid. On the four selected days the calculated sulfuric acid concentrations ranged from  $1 \times 10^6$  to  $2 \times 10^7$  molecules  $\text{cm}^{-3}$  inside the mixed layer. This range is typical for the SMEAR II station in Hyytiälä, as pointed out by Boy et al. (2005).

The noon-time vertical profiles of the four parameters calculated by MALTE as an input for PARNUC are shown in Fig. 1. Also included in this figure are the vertical profiles of ionization rates, concentrations of hydroxyl radicals and sulfur dioxide, and for comparison the noon-time measured sounding profiles of temperature, potential temperature and specific humidity from Jokioinen.

### 4. Results and discussion

Measured and modeled aerosol number concentrations of particles with diameters  $> 3 \text{ nm}$  at ground level for the four considered days are shown in Fig. 2. The model runs were performed using either kinetic or activation type nucleation to predict the number of newly formed clusters. The results show that the onset of particle formation and the maximum number

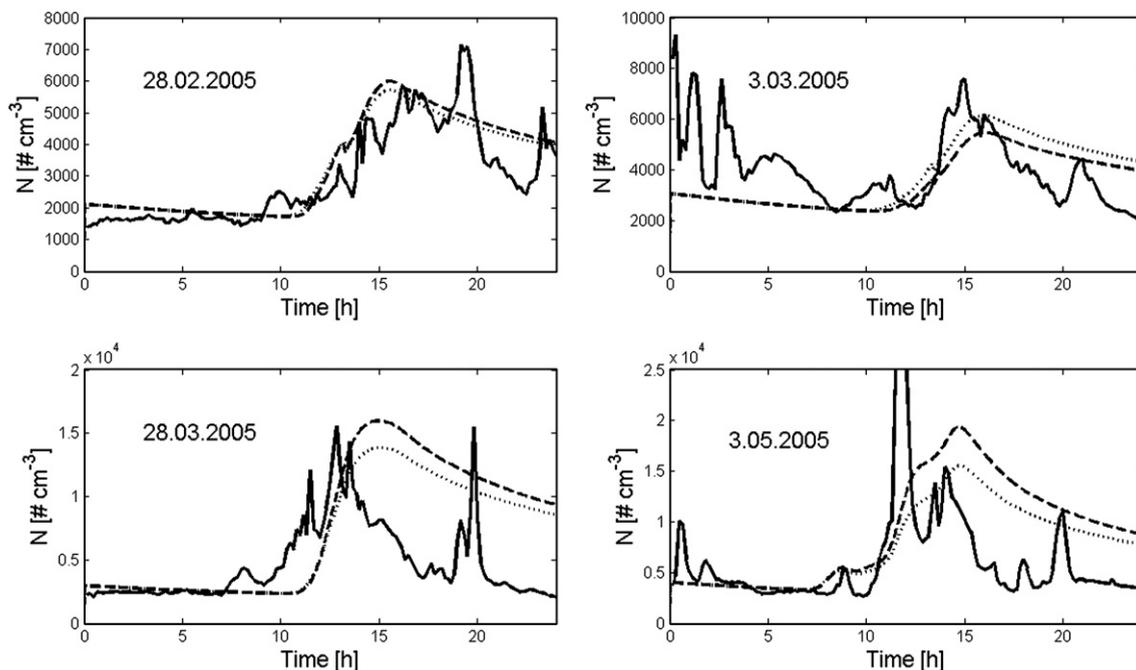


Fig. 2. Measured and modeled total particle number concentration for all selected days; dashed and dotted lines denote modeled values calculated by kinetic and activation theory, respectively; solid lines represent measurements.

concentrations in the model agree well with the measurements. There is no systematic bias in the model results, over-or under-predicting the observed particle concentrations. The differences between simulated and measured particle concentrations likely reflect the fact that the *A*- and *K*-coefficients in Eqs. (1) and (2) are empirical estimates, and the horizontal in-homogeneity of the real atmosphere due to advection, unaccounted for in the one-dimensional model MALTE. The effect of horizontal advection is most obvious on the 3rd of March, where the total particle number concentration decreases during the first 5 h by a factor of 2, probably related to the arrival of a clean air mass at the station. On this day we used the size distribution measured in the early morning (instead of at midnight) for the model initialization, in order to obtain correct CS values at the time when new particle formation was observed at the station.

In order to assess the fraction of the newly formed aerosol that is formed due to IINSW, we performed 5 model runs for each day, using single and combination of nucleation mechanisms in each run:

- run A — kinetic nucleation
- run B — activation type nucleation

- run C — IINSW
- run D — kinetic nucleation and IINSW
- run E — activation type nucleation and IINSW

The disadvantage of runs A to C is its neglect coagulation between the smallest particles produced by different nucleation mechanisms: consequently, run C (IINSW only) will produce only an upper limit to the actual contribution of IINSW to the observed particle concentrations, but presents a more independent picture about the relevance of IINSW. Model simulations by run D and E showed that the loss of newly formed particles due to coagulation in the smallest size ranges is in the order of 20%, which was already pointed out in an earlier publication by [Wehner et al. \(2005\)](#).

Fig. 3a presents vertical profiles of number concentrations of particles in the size range 3–10 nm simulated with (mean value from run A+B and adding run C) and without IINSW (mean value from run A+B) for the first 2 km above ground. In Fig. 3b the ratio of particles in the same size range produced by IINSW (run C) to the mean values of particles produced by run A and B are presented. During the first day (28th of February) the temperature was below freezing throughout the troposphere and the air masses were less polluted compared

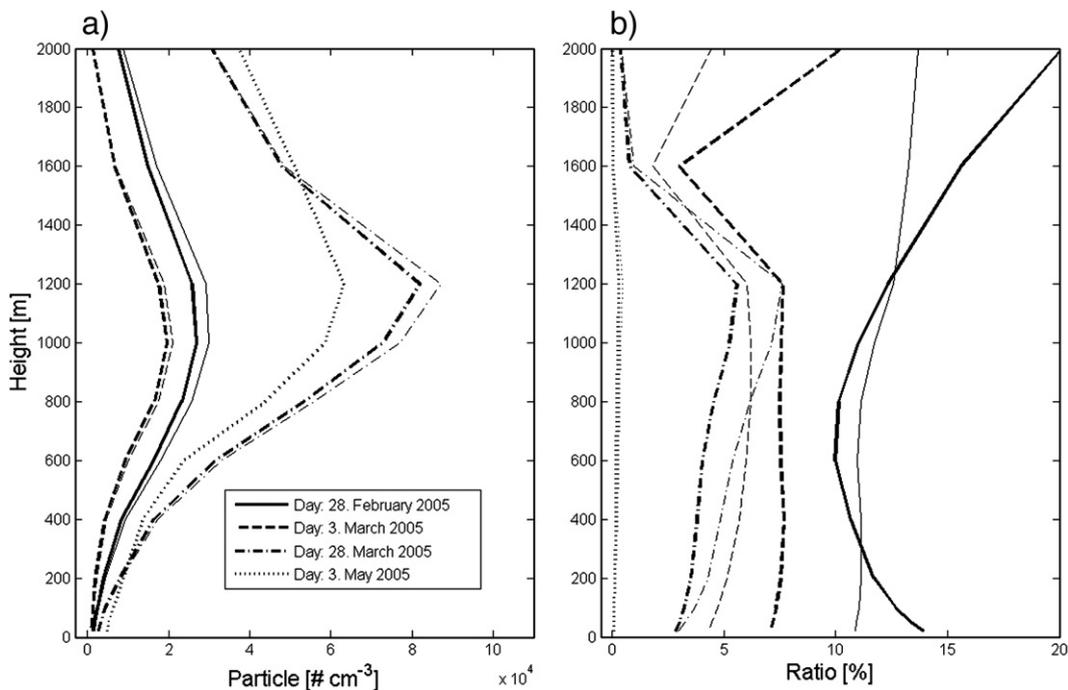


Fig. 3. Vertical profiles of particles between 3–10 nm for the selected days during the first 3 h after nucleation was observed at 3 nm: a) Mean values calculated by kinetic and activation theories (thick lines), adding the number from IINSW (thin lines) b) Ratio of particles produced by ion-induced nucleation to kinetic nucleation (thick lines) and activation theory (thin lines).

with the other days. Although sulfuric acid concentrations were 2–8 times lower on this day compared to the two days with the strongest formation events, the production of new particles from IINSW reaches the highest values, with a contribution around 12% inside the mixed layer. The next day exhibited similar meteorological conditions; the  $\text{SO}_2$  concentrations however were 3–4 times lower compared to the other days. On this day ion induced nucleation of sulfuric acid and water contributes approximately 5–7% to the total amount of particles formed inside the boundary layer. The 28th of March was more polluted compared with the two preceding days, based on the calculated CS values; temperatures in the mixed layer were around freezing and sulfuric acid concentrations highest from all the selected days. IINSW contributed 3–5% compared to kinetic and activation mechanisms throughout the mixed layer. The last simulated day showed positive temperatures inside the boundary layer, and although the other parameters were close to values of the earlier days, the IINSW contribution to newly formed particles was less than 0.5%.

The results indicate the strong dependence of the IINSW parameterization on temperature and sulfuric acid concentrations. Temperatures below  $0\text{ }^\circ\text{C}$  and  $\text{H}_2\text{SO}_4$  concentrations above  $1 \times 10^6$  molecules  $\text{cm}^{-3}$  could result in particle production by IINSW up to several 1000 particles  $\text{cm}^{-3}$  in the nucleation mode and could contribute a significant fraction to observed particle formation events. However, on days with

temperatures above freezing (most observed event days in Hyytiälä) the IINSW seems to be negligible as far as new particle formation in the planetary boundary layer is concerned. This is consistent with recent results (Iida et al., 2006) from a field campaign near Boulder, Colorado, USA, showing a contribution of ion induced nucleation of only 0.5% on average to the total amount of newly formed particles (13 from the 14 experiment days featured temperatures between  $10\text{--}30\text{ }^\circ\text{C}$ ).

Above the mixed layer, within the free troposphere, the simulations predict higher particle concentrations due to ion-induced nucleation on the last two days (see Fig. 4). However, the high uncertainties in the vertical structure of the input parameters (in particular the profiles of preexisting aerosol particles and inorganic compounds, such as sulfur dioxide, ozone, nitrogen oxides, etc.) translate into uncertainties in the model results and underscore the need for more measurements inside the free troposphere. At the same time, the  $A$ - and  $K$ -coefficients used to describe the kinetic and activation nucleation theories have so far been determined only empirically from near-surface measurements. The theoretical framework for their calculation, as well as for the calculation of the partitioning of organic molecule oxidation products – which may give a strong decrease of the  $A$ - and  $K$ -coefficients above the mixed layer – has yet to be developed. For these reasons we present only the vertical distribution of particles in the size range between 3 and 10 nm produced from IINSW in Fig. 4. These results show pronounced peaks in the

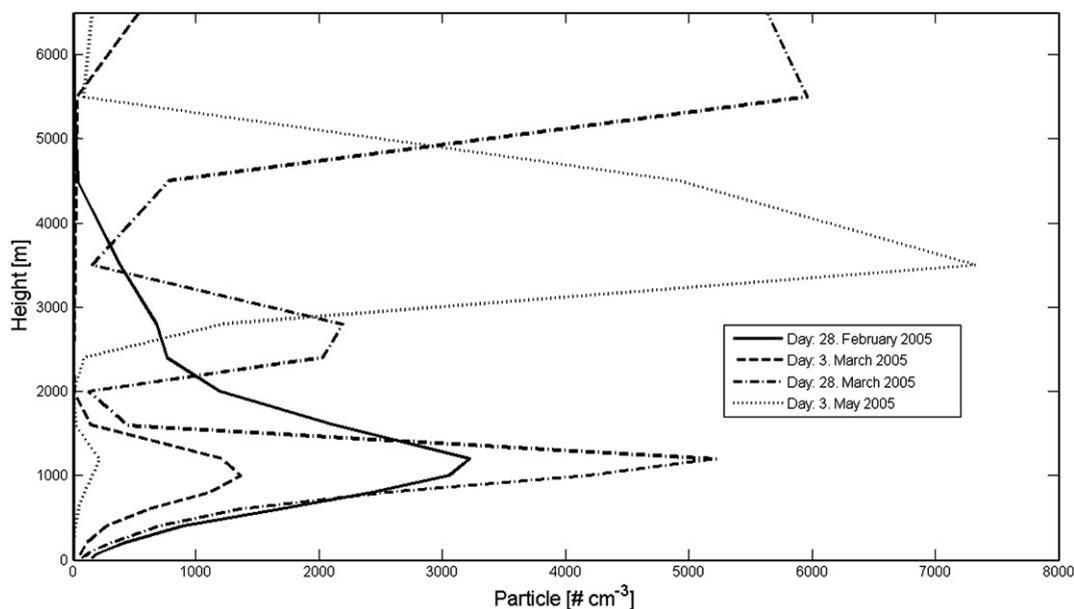


Fig. 4. Vertical profiles of particles (3–10 nm) calculated by IINSW as mean values for 3 h after nucleation was observed at 3 nm for the 4 selected days.

concentration of the particles in the selected size range on the days with high H<sub>2</sub>SO<sub>4</sub> concentrations in the free troposphere. This indicates that IINSW could be a very important mechanism for new particle formation in the free troposphere even on days where IINSW makes a negligible contribution to the total amount of new formed particle inside the mixed layer.

## 5. Conclusions

In this work we combined two independently developed models (MALTE and PARNUC) to investigate the relevance of ion-induced nucleation of sulfuric acid and water in the lower troposphere over the boreal forest in Northern Europe. Our simulations, covering four days with nucleation events, and using measured atmospheric input data from the SMEAR II station in Hyttälä, reproduce observed particle concentrations reasonably well, and are in good agreement with earlier publications on this topic at ground level (Eisele et al., 2006). On the four simulated days, IINSW contributes between <0.5 to 12% to the total amount of new formed particles inside the mixed layer, depending on environmental parameters including sulfuric acid concentration, temperature, preexisting aerosol condensational sink, and relative humidity. Because the *A*- and *K*-factors used in this work to describe the kinetic and activation type nucleation mechanisms have been determined empirically only from near-surface observations, a comparison of the relative contributions of these mechanisms and of IINSW to new particle formation would be to hypothetical in the free troposphere above the mixed layer. Notwithstanding the uncertainties introduced by the estimated trace gas concentration and pre-existing aerosols profiles in the free troposphere, the results indicate that IINSW could be an important aerosol formation mechanism in the free troposphere even on days where its contribution to new particle formation inside the mixed layer is negligible, which is consistent with the results published recently by Kazil et al. (2007).

Based on the model simulations presented in this work we conclude that ion-induced nucleation of sulfuric acid and water is a negligible source of newly formed particles inside the mixed layer over the boreal forest at northern latitudes when temperatures are above freezing. Our results are based on model simulations from early spring 2005 and can only be used as an indicator concerning the relevance of IINSW in the lower troposphere of the boreal forest at northern latitudes. Contributions of other molecules like organics or NH<sub>3</sub> mentioned in a recent publication by Yu and co-workers (2006) are not considered in this manuscript but should be investigated

in the future. Additional studies are needed to determine to what extent our simulations are representative for the boreal forest worldwide over the whole year and how important IINSW is in the free troposphere.

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