

Supplementary Materials

Method for Automated Estimation of Parameters Controlling Aerosol New Particle Formation

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Description of the Simulator

In the present study, the simulator version HT20060912 is used (Tammet and Kulmala 2005; 2007). It has 61 physical input parameters and many technical parameters that control program flow, program output *etc.*. Twelve physical parameters can have dual values: for free air and for forest environment. Several input parameters are given for initial, halftime (midpoint) and final time points. The actual values of these parameters at particular time points within the simulation interval are interpolated from these initial, halftime and final values using a parabolic trend. Nucleation rates are given by the maximum values. The actual nucleation rates at particular time points are calculated as the product of the maximum rates and a nucleation variation function, determined by additional parameters. Next we present the complete list of the physical input parameters with short descriptions.

1: Time period under consideration (up to 1440 min)

2: Number of evolution steps in a minute, n (a technical parameter). Time step is $60/n$ seconds when calculating the evolution of ions and particles. The computing time is proportional to square of n . The number of size sections will be determined by the program and it is proportional to the number of evolution steps.

3: Acceleration coefficient (a technical parameter). A multiplier to the section width, which decreases the computation time and accuracy.

4: Air temperature

5: Air pressure

6: Initial ionization rate (dual value parameter, one value for free air and another value for forest environment)

7: Halftime ionization rate (dual value parameter).

8: Final ionization rate (dual value parameter).

The actual values (one for free air and another for forest environment) of the ionization rates at particular time points within the simulation interval are interpolated from these three values using a parabolic trend.

9: Electric mobility of positive cluster ions.

10: Electric mobility of negative cluster ions.

11: Cluster ion mutual recombination coefficient.

12: Density of ions. The density has a minor effect on the results via the small ion size-mobility conversion.

13: Birth size of particles. The nucleation is considered as a genesis of particles of a given size. If the birth size is defined as very small, then it may happen that the particles will not grow at due to the quantum rebound and/or nano-Köhler process. The parameters of the growth are presented when describing the condensing substances.

14: Maximum nucleation rate for positive ion nucleation (dual value parameter).

15: Maximum nucleation rate for negative ion nucleation (dual value parameter).

16: Maximum nucleation rate for neutral nucleation (dual value parameter).

The actual nucleation rates for free air and forest environment are calculated as the product of the maximum rates and the nucleation variation function that is common for positive, negative, and neutral nucleation. The variation function begins and ends with zero and is described using the following five parameters.

17: Rise time of the nucleation activity, $t1$.

18: Shape code of rise: 1=linear, 2=sinus, 3=square_of_sinus. The argument of the sine is zero at the beginning of the rise phase and $\pi/2$ at the end of the rise phase.

19: Time of steady nucleation activity, $t2$.

20: Time of dropping nucleation activity, t_3 . Nucleation rate decreases from the maximum value until zero.

21: Shape of dropping: 1=linear, 2=sinus, 3=square_of_sinus. The argument of sine is $\pi/2$ at the beginning of dropping and 0 at the end. The total duration of nucleation is equal to sum $t_1 + t_2 + t_3$.

Parameters 22–39 control growth of the particles, arisen by nucleation. Growth proceeds by two different condensing substances.

22: Density of growth units. This value has a minor effect on the results via the diffusion coefficient of growth units.

23: Extra distance of the Van der Waals capture.

24: Diameter of a growth unit.

25: Polarizability. Polarizability of a conducting sphere is $(d/2)^3$. The polarization effect can be ignored when writing here 0.

26: Nadykto-Yu dipole enhancement factor for $d = 1$ nm. Nadykto and Yu presented a model of permanent dipole effecting condensation. If the method of effective polarization is used, then the Nadykto-Yu factor must be bypassed assigning the value 1 to the factor as at $d = 1$ nm as well at $d = 2$ nm.

27: Nadykto-Yu dipole enhancement coefficient for $d = 2$ nm.

28: Initial plain Knudsen growth rate of neutral particle (dual value parameter). The actual value of the plain growth rate at particular time points within the simulation interval are interpolated from these three values using a parabolic trend. The plain Knudsen growth rate neglects the interception size of growth units, Van der Waals capture, polarization effect and quantum rebound of growth units. The measurable growth rates differ from the plain ones by specific size dependent factors that also take into account the abovementioned effects (Van der

Waals capture etc.); the values of the factors are computed as a part of the simulation process and are usually between 1 and 1.5, see (Tammet and Kulmala, 2005). The plain growth rates are used as simulator input parameters, within the simulation process they are always modified by the abovementioned factors, which results in the values, comparable to the measurable growth rates.

29: Halftime plain Knudsen growth rate of neutral particles (dual value parameter).

30: Final plain Knudsen growth rate of neutral particles (dual value parameter).

31: Critical size of quantum rebound.

32: Extra temperature of quantum rebound.

Parameters 22–32 describe the first condensing substance (e.g. sulphuric acid), responsible for initial particle growth. The first substance is expected to be non-evaporating. The condensation may be retarded at extra low sizes by the quantum rebound of growth units.

33: Diameter of a growth unit.

34: Polarizability.

The Nadykto-Yu factor cannot be applied for the second condensing substance and the effect of permanent dipole can be included using the method of effective polarizability.

35: Initial plain Knudsen growth rate of neutral particles (dual value parameter).

36: Halftime plain Knudsen growth rate of neutral particles (dual value parameter).

37: Final plain Knudsen growth rate of neutral particles (dual value parameter).

38: Critical diameter when the condensation starts.

39: Power of nano-Koehler approximation.

Parameters 33–39 describe the second condensing substance (e.g. some organic compound), responsible for the ongoing accelerated particle growth. The condensation is expected to follow the approximated nano-Köhler law.

40: Initial average diameter of background aerosol particles.

41: Halftime average diameter of background aerosol particles.

42: Final average diameter of background aerosol particles.

43: Initial concentration of background aerosol particles.

44: Halftime concentration of background aerosol particles.

45: Final concentration of background aerosol particles.

The actual values of the characteristics of the background aerosol particles at particular time points within the simulation interval are interpolated from the parameters 40–45 using a parabolic trend.

46: Air residence distance (time×wind) in forest.

47: Initial wind in the forest.

48: Halftime wind in the forest.

49: Final wind in the forest.

50: Conifer needle diameter.

51: Conifer needle length in a unit volume m/m³.

Wind speed and the needle parameters are important only in the calculation of dry deposition in the forest. If the measurement site is not in the forest, then the needle length should be written 0 and other forest parameters may have arbitrary values. The actual values of the wind at particular time points within the simulation interval are interpolated from the parameters 47–49 using a parabolic trend.

Algorithm for calculating the estimates of NPF parameters

The principle of the combinations from the particular input vectors is now illustrated by an example. Let us have three vectors, which contain 4 elements (actually, we have 5 vectors with 61 elements). Each one from these three vectors contains just one modified parameter from the list (1x, 2x, 3x, 4x) and three initial (not modified) parameters from the list (1, 2, 3, 4). Let the

three vectors be (1x, 2, 3, 4); (1, 2x, 3, 4) and (1, 2, 3, 4x). Then there will be 7 combinations (1x, 2, 3, 4); (1, 2x, 3, 4); (1, 2, 3, 4x); (1x, 2x, 3, 4); (1x, 2, 3, 4x); (1, 2x, 3, 4x) and (1x, 2x, 3, 4x). The actual case is similar: each from the five vectors contains one modified element and 60 elements have been not modified. In the actual case, we obtain 31 combinations. Next, the algorithm simulates all the particular cases, defined by the 31 combinations, and for every particular case computes the corresponding measure of difference.

Characteristics of test data

For the simulation of a NPF event, it is necessary to establish the onset time of the event. For this purpose we examined the graphs of the concentrations of measured nanoparticles and selected the time point, when a considerable rise in the concentrations of these nanoparticles began. As seen in the Fig S1(a), a considerable rise in the concentrations of "natural" and "bipolar" ions started at about 8:00, but this is not the proper onset time. A burst should start from particles with sizes of about 1 nm (Kulmala *et al.*, 2013), but the measured low end of DMPS particle diameter range was 2.8 nm, therefore the instruments do not see the particles that emerge just at the onset of a burst. In case we take the growth rate of nanoparticles for this size region to be between 1 and 2 nm/h (as found by Kulmala *et al.*, 2013), we can assume an about 1 hour earlier burst onset time for about 1 nm size particles. Thus we chose a 1-hour earlier onset times, 7:00 for case 1 and 8:00 for case 2.

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Table S1(a). Measured meteorological and background aerosol parameters at the SMEAR II station, Hyytiälä, on 7 April 2000. Column “LST” presents the time, when the particular parameter was measured. LST is the local standard time (standard time for Finland or UTC + 2 hours). “Initial, midpoint and final” mark the corresponding points in the simulated time interval. In Tammet and Kulmala (2005; 2007) “midpoint” is referred as “halftime”. Abbreviation BP marks background aerosol particles larger than 8.6 nm.

Parameter	LST	Value	Unit
Air temperature	11:30	4.0	Celsius
Air pressure	11:30	1001	millibar
Initial average diameter of BP	07:00	36.4	nm
Midpoint average diameter of BP	11:30	23.1	nm
Final average diameter of BP	16:30	24.5	nm
Initial concentration of BP	07:00	1540	cm ⁻³
Midpoint concentration of BP	11:30	4380	cm ⁻³
Final concentration of BP	16:30	6140	cm ⁻³

Table S1(b). Measured concentrations of nanoparticles and cluster ions (in cm^{-3}) at the SMEAR II station, Hyytiälä, on 7 April 2000. Column “LST” contains the local standard time (standard time for Finland or UTC + 2 hours). Column “Time” presents times, in minutes, elapsed from the start of the NPF event. These time points are also given in Fig. 2a, which presents the detailed graphs. Column with notation “n-“ refers to the concentrations of negative cluster ions in the size range of 0–1.9 nm, the actual values are divided by 100; “N-“ is the concentrations of negative nanoparticles, the actual values are divided by 10; “No” is the concentrations of neutral nanoparticles, the actual values are divided by 500; all the notations are in line with the ones, used in the simulation tool. The size range of nanoparticles is 2.8–8.6 nm. Values in columns “n-“, “N-“ and “No” are used as test data.

LST	Time	n-/100	N-/10	No/500
7:00	0			
7:30	30	7.57	0.6	0.429
8:00	60	7.18	0.35	0.367
8:30	90	7.08	2.15	0.639
9:00	120	6.64	2.15	1.202
9:30	150	6.15	2.08	1.658
10:00	180	5.88	3.35	2.60
10:30	210	5.61	3.73	2.462
11:00	240	4.93	6.06	4.019
11:30	270	5.05	7.10	4.792
12:00	300	4.97	6.21	3.841
12:30	330	4.97	5.93	3.234
13:00	360	4.79	3.61	2.136
13:30	390	4.70	2.56	1.527
14:00	420	4.89	3.28	1.731
14:30	450	4.83	2.00	1.371
15:00	480	4.97	1.98	1.141
15:30	510	4.84	1.87	0.945
16:00	540	4.37	0.96	0.510
16:30	570	4.33	0.57	0.408
Average		5.46	2.98	1.843

Table S2(a). Measured meteorological and background aerosol parameters at the SMEAR II station, Hyytiälä, on 8 April 2000. The notations are the same as in Table 1a.

Parameter	LST	Value	Unit
Air temperature	11:00	3.5	Celsius
Air pressure	11:00	1006	millibar
Initial average diameter of BP	08:00	50	nm
Midpoint average diameter of BP	11:00	22	nm
Final average diameter of BP	14:30	21.3	nm
Initial concentration of BP	08:00	1310	cm ⁻³
Midpoint concentration of BP	11:00	5000	cm ⁻³
Final concentration of BP	14:30	15300	cm ⁻³

Table S2(b). Measured concentrations of nanoparticles and cluster ions (in cm^{-3}) at the SMEAR II station, Hyytiälä, on 8 April 2000. Fig. 2b presents the detailed graphs. The notations are the same as in Table 1b. Values in columns “n–“, “N–“ and “No” are used as test data.

LST	Time	n–/100	N–/10	No/500
08:00	0			
08:30	30	6.12	1.49	0.3
09:00	60	5.97	0.96	0.373
09:30	90	5.56	2.53	0.974
10:00	120	5.24	3.1	0.979
10:30	150	4.94	7.85	2.876
11:00	180	4.62	7.49	2.732
11:30	210	4.12	6.08	2.107
12:00	240	4.02	7.4	3.903
12:30	270	3.77	8.78	3.361
13:00	300	3.56	5.16	1.709
13:30	330	3.67	5.44	2.547
14:00	360	3.04	2.04	0.844
14:30	390	3.23	1.99	1.549
Average		4.45	4.64	1.866

Figure captions

Fig. S1(a). Diurnal evolution of the particular fractions (cm^{-3}). These fractions are used as test data within the present study. Figure depicts the evolution of negatively charged aerosol particles and negative small ions at SMEAR II Station, Hyytiälä, Finland, on 7 April 2000 (case 1). “Natural” denotes naturally charged particles in a diameter range of 2.8–8.6 nm, “Bipolar” denotes particles in the same size range charged in the bipolar charger, and “n” cluster air ions measured by means of air ion counters. LST is the local standard time (standard time for Finland or UTC + 2 hours).

Fig. S1(b). Diurnal evolution of particle size distribution for case 1.

Fig. S2(a). Diurnal evolution of the particular fractions (cm^{-3}). These fractions are used as test data within the present study. Figure depicts the evolution of negatively charged aerosol particles and negative small ions at SMEAR II Station, Hyytiälä, Finland, on 8 April 2000 (case 2). The notations are the same as in Fig S1(a).

Fig. S2(b). Diurnal evolution of particle size distribution for case 2.

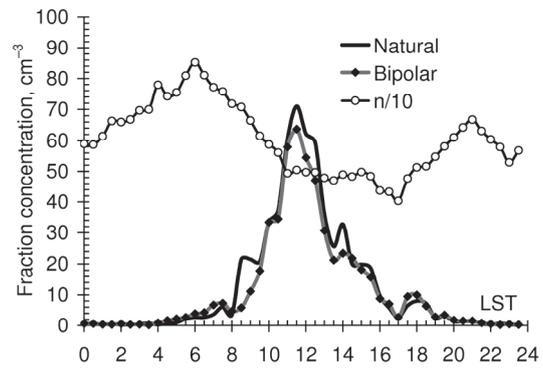


Fig. S1(a).

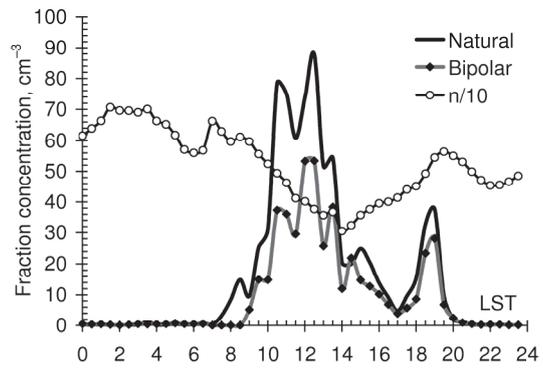


Fig. S2(a).

DMPS, Hyytiälä, 07-Apr-2000

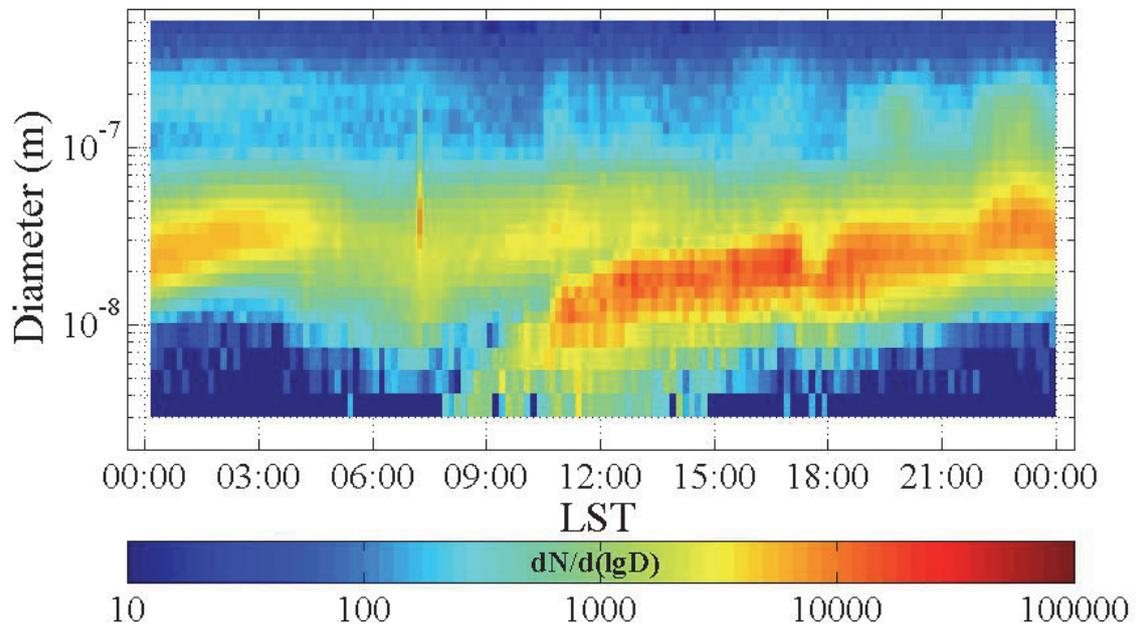


Fig. S1(b).

DMPS, Hyytiälä, 08-Apr-2000

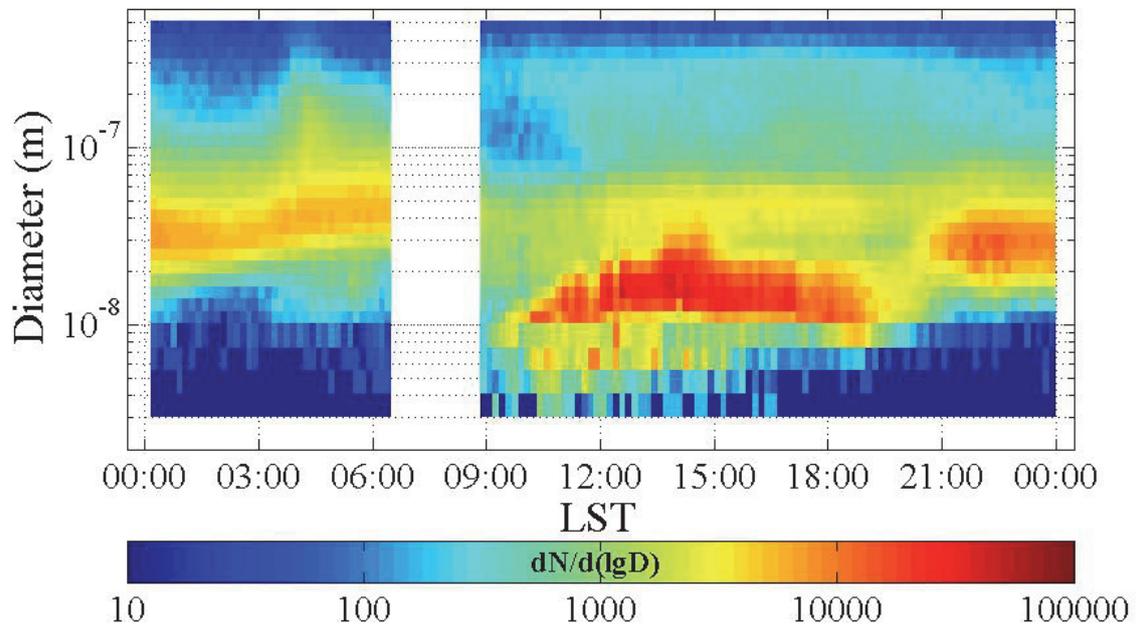


Fig. S2(b).

Appendix S1. Algorithm of the calculations of the fraction concentrations of neutral nanoparticles.

The database of DMPS measurements was converted into Excel tables with the fraction concentrations of particles in 29 diameter intervals. The geometrical midpoints of the intervals extended from 3.03 nm to 495 nm. There were the tables with the fraction concentrations of negative particles $N_{\text{Nat},j}$ and $N_{\text{Bip},j}$ and also a table with the total fraction concentrations of aerosol particles N_j in the certain size range calculated from $N_{\text{Bip},j}$ by means of the ordinary algorithm of DMPS used at the SMEAR II station. The subscript j enumerates the size fractions. The fraction concentrations of naturally charged negative particles $N_{\text{Nat},j}$ and bipolar charged negative particles $N_{\text{Bip},j}$ were measured by means of two different DMPS as described above. The concentrations of the first four fractions $N_{\text{Nat},j}$ were summed up, giving us the concentration of negative nanoparticles in the diameter interval of 2.8–8.6 nm, N^- .

The fraction concentrations of neutral nanoparticles were not directly available. These concentrations were estimated through approximate calculations as follows. In principle, the concentration of neutral nanoparticles of a given size fraction $N_{0,j}$ equals to the total concentration of this size fraction N_j (neutral + charged particles) subtracted by the concentrations of charged particles. We supposed that the concentration of charged particles equals to $2 \times N_{\text{Bip},j}$. As the last mentioned concentration is considerably less than the total concentration, the uncertainty of the calculations is reduced. The concentrations of the first four fractions $N_{0,j}$ were also summed up in order to get the concentration of neutral nanoparticles in the diameter interval of 2.8–8.6 nm, N_0 .