Supplementary materials

Interpretation of Atmospheric Aerosol Measurements by Means of a Numerical Simulator of New Particle Formation Events

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Method for the estimation of NPF parameters

General flowchart of the estimation algorithm is presented in Fig. S1. The full estimator package and further support is available by contacting the authors. Next we present certain comments about this flowchart.

Main characteristics of the NPF events

The meteorological and the detailed background aerosol parameters are presented in Tables S1–S7.

Parameters and constraints used in the estimations

The concentrations of negatively charged nanoparticles and negative cluster ions were directly measured. The fraction concentration of neutral nanoparticles in the same size range was calculated using the measured data of bipolar charged (or neutralized) particles. The particular algorithm of these calculations is presented in Appendix S1.

By default, the simulator contains 61 free physical input parameters. Several parameters are fixed; as a result we estimated 39 physical parameters. The complete list of the parameters of simulator is presented in Appendix S2. Next we describe the applied constraints more in detail.

Recombination coefficient of cluster ions was assumed $1.6 \cdot 10^{-6}$ $cm^{-3}s^{-1}$. Certain microphysical parameters, which determine the collision interaction between molecules, ions and particles as explained by Tammet and Kulmala (2005) were also fixed in simulations: density of cluster ions 2 g cm^{-3}, polarizability of the first growth units 149 $Å^3$, polarizability of the second growth units 32 $Å^3$, extra distance of Van der Waals capture 0.115 nm, Nadykto-Yu enhancement factors of dipole moment on the coagulation coefficient at two fixed sizes of 1 and 2 nm are both equal to 1, critical size of quantum rebound 2.75 nm, temperature of quantum rebound 500 K, and power of nano-Köhler approximation 2 (the nano-Köhler model describes an initial growth of nucleated particles; first only by the condensation of sulfuric acid until the particles reach a diameter where low volatile organic vapors can start contributing to their growth). Polarizabilities could help to identify the substance that is responsible for the particular nucleation burst. Because of that, these parameters should in principle be free. Nevertheless, according to our simulation experiments,

the burst simulator is almost insensitive to these parameters. Therefore, the optimization algorithm cannot be driven effectively by these parameters and we used the values, proposed by Tammet and Kulmala (2005; 2007).

In the simulator, conifer forest is characterized by six independent input parameters. Variations in some parameters can be compensated by variations in others. To simplify calculations, it is desirable to fix several forest parameters. Tammet *et al*. (2006) assumed the average conifer needle to be 0.9 mm. On the basis of optimizations and direct measurements of the needles, we estimated that the average diameter could be 1.5 mm and then we fixed it. The preliminary optimizations of the burst event on 8 April resulted in a value for the conifer needle length in a unit volume ($m \cdot m^{-3}$) equal to 155. We regarded this value as plausible and further fixed it. This way we kept only one parameter, which determines how many trees an air parcel meets when moving through the forest; it is the "air residence distance in forest". Following a moving air parcel, the features of the forest it passes can depend on the wind direction. Therefore, in case the wind blows from a particular direction, the values of the "air residence distance" can differ from the value for the case when the wind blows from another direction. The values of the "air residence distance" obtained for different days (different wind directions) can be compared and evaluated in respect of the features of the forest in the particular directions. In Tammet and Kulmala (2007) the term "air residence time in forest" is used. If we multiply the residence time by the wind speed, then we obtain the residence distance.

The nucleation burst simulator is sensitive to the values of ionization rates. In accordance with the preliminary calculations, the optimization can result in diverse values. However, the ionization rates are expected to be significantly higher than those found for the marine environment (about 2 $cm^{-3}s^{-1}$), even though several studies reported the values of about 2.5 $cm^{-3}s^{-1}$ also for continental stations (Laakso *et al.* 2004). For that reason in our previous paper we set the constraint that the ionization rates cannot be below 4.0 $cm^{-3}s^{-1}$. This value matches well with the average values of 5.6 $cm^{-3}s^{-1}$ and 3.9 $cm^{-3}s^{-1}$, found respectively for the same place at the 2 m and 14 m heights from the ground level by Tammet *et al.* (2006).

Growth rate

Summary of the results obtained from previous numerous research campaigns carried out mainly at Hyytiälä, Finland is given in main text, Table 3. Here we present a textual overview. Dal Maso *et al*. (2005) analyzed the aerosol measurements at a boreal forest site at Hyytiälä, Finland, between 1996 and 2003. They found that the mean growth rate of the nucleation mode particles was 3.0 $nm \cdot h^{-1}$, peaking in summer. Hirsikko *et al*. (2005) analyzed the measurements performed at Hyytiälä during April 2003–April 2004, and obtained a clear size-dependent growth rate for nanometer particles: the median diameter growth rates for the size classes 1.3–3 nm, 3–7 nm and 7–20 nm were on average 1–2 nm h^{-1}, 2–4 nm h^{-1} and 4–5 nm h^{-1}, respectively. The growth rates of the ions or particles in the smallest size class were almost independent of the season, while the larger particles had a clear annual cycle with the highest values recorded during summer and lowest values during winter. This annual cycle can be attributed to the elevated concentrations of volatile organic compounds (VOC) in the air. Manninen *et al*. (2009) analyzed the measurements carried out during the EUCAARI field campaign at Hyytiälä in spring 2007; the median growth rate of particles in a size class of 3–7 nm was 3.8 $nm \cdot h^{-1}$. Yli-Juuti *et al*. (2011) studied the diameter growth rates of nucleation mode particles during the years 2003–2009 at the SMEAR II in Hyytiälä. They found that the median growth rates in particle diameter ranges of 1.5–3 nm and 3–7 nm were 1.9 $nm \cdot h^{-1}$ and

3.8 $nm \cdot h^{-1}$, respectively. Gagné *et al.* (2012) measured aerosols by means of an Ion-DMPS in Helsinki, Finland between December 2008 and February 2010. The growth rates in the 3–7 nm size range for class I events varied between 3.2 and 7.5 $nm \cdot h^{-1}$. Vuollekoski *et al*. (2012) performed an analysis of a nucleation burst that was recorded at Hyytiälä on 1 April 2003. The result for the growth rate of nanometer particles was an average value of 3.4 $nm \cdot h^{-1}$. Considering these results, we may conclude that the growth rate values obtained by our simulations for the particle size interval 2.8–8.6 nm are close to the results known elsewhere.

Charging state

Detailed calculations for a particular NPF event are given in Table S8.

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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 $N_{Nat,j}$ and $N_{Bip,j}$ and also a table with the total fraction concentrations of aerosol particles N_j in the certain size range calculated from $N_{Bip,j}$ 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 $N_{Nat,j}$ and bipolar charged negative particles $N_{Bip,j}$ were measured by means of two different DMPS as described above. The concentrations of the first four fractions $N_{Nat,j}$ 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 No,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 $2\times N_{Bip,j}$. 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 No,j were also summed up in order to get the concentration of neutral nanoparticles in the diameter interval of 2.8–8.6 nm, No.

Appendix S2. The parameters of the simulator.

In the present study, the simulator version HT20060912 is used (Tammet and Kulmala 2005; 2007). The burst simulator program (without the estimator software) is freely available on the web http://code.google.com/p/aerosol-genesis-simulator/downloads/list. It has 61 physical input parameters and a number of technical parameters that control program flow, program output etc.. Twelve physical parameters can have dual values: one for free air and other for forest environment. The values for free air and for forest environment can be different. Several input parameters are given for initial, halftime (midpoint) and final time points. The actual values of these time-dependent 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 also time-dependent, they 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 (by the parameters No 17–21). Next we present the complete list of the physical input parameters with short descriptions. List items No 6, 7, 8, 14, 15, 16, 28, 29, 30, 35, 36 and 37 describe dual-value parameters. The list also contains two technical parameters (No 2 and 3).

1 (fixed): Time period under consideration (up to 1440 min)
2 (fixed): 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 (fixed): Acceleration coefficient (a technical parameter). A multiplier to the section width, which decreases the computation time and accuracy.

4 (fixed): Air temperature
5 (fixed): Air pressure
6 (free): Initial ionization rate (dual value parameter, one value for free air and another value for forest environment)
7 (free): Halftime ionization rate (dual value parameter).
8 (free): 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 (free): Electric mobility of positive cluster ions.
10 (free): Electric mobility of negative cluster ions.
11 (fixed): Cluster ion mutual recombination coefficient.
12 (free): Density of ions. The density has a minor effect on the results via the small ion size-mobility conversion.
13 (free): 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 (free): Maximum nucleation rate for positive ion nucleation (dual value parameter).
15 (free): Maximum nucleation rate for negative ion nucleation (dual value parameter).
16 (free): 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 (free): Rise time of the nucleation activity, t1.
18 (fixed): 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 (free): Time of steady nucleation activity, t2.
20 (free): Time of dropping nucleation activity, t3. Nucleation rate decreases from the maximum value until zero.
21 (fixed): 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 t1+ t2+ t3.
Parameters 22–39 control growth of the particles, arisen by nucleation. Growth proceeds by two different condensing substances.
22 (free): Density of growth units. This value has a minor effect on the results via the diffusion coefficient of growth units.
23 (fixed): Extra distance of the Van der Waals capture.
24 (free): Diameter of a growth unit.
25 (fixed): Polarizability. Polarizability of a conducting sphere is (d/2)3. The polarization effect can be ignored when writing here 0.
26 (fixed): Nadykto-Yu dipole enhancement factor for d = 1nm. 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 (fixed): Nadykto-Yu dipole enhancement coefficient for d = 2 nm.
28 (free): 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 (free): Halftime plain Knudsen growth rate of neutral particles (dual value parameter).
30 (free): Final plain Knudsen growth rate of neutral particles (dual value parameter).
31 (fixed): Critical size of quantum rebound.
32 (fixed): 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 (free): Diameter of a growth unit.
34 (fixed): 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 (free): Initial plain Knudsen growth rate of neutral particles (dual value parameter).
36 (free): Halftime plain Knudsen growth rate of neutral particles (dual value parameter).
37 (free): Final plain Knudsen growth rate of neutral particles (dual value parameter).
38 (free): Critical diameter when the condensation starts.
39 (fixed): 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 (fixed): Initial average diameter of background aerosol particles.
41 (fixed): Halftime average diameter of background aerosol particles.
42 (fixed): Final average diameter of background aerosol particles.
43 (fixed): Initial concentration of background aerosol particles.
44 (fixed): Halftime concentration of background aerosol particles.
45 (fixed): 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 (free): Air residence distance (time×wind) in forest.
47 (free): Initial wind in the forest.
48 (free): Halftime wind in the forest.
49 (free): Final wind in the forest.
50 (fixed): Conifer needle diameter.
51 (fixed): 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.

TABLES

Table S1a. Measured meteorological and background aerosol parameters at the SMEAR II station, Hyytiälä, on 29 March 2000. Column "LST" presents the time, when the particular parameters were measured. "Initial, halftime and final" mark the corresponding points in the simulated time interval. Abbreviation BP marks background aerosol particles larger than 8.6 nm.

Parameter	LST	Value	Unit
Air temperature	13:00	3.1	Celsius
Air pressure	13:00	1003	millibar
Initial average diameter of BP	08:30	55	nm
Halftime average diameter of BP	13:00	24	nm
Final average diameter of BP	17:30	33,0	nm
Initial concentration of BP	08:30	3360	cm^{-3}
Halftime concentration of BP	13:00	13200	cm^{-3}
Final concentration of BP	17:30	6710	cm^{-3}

Table S1b. Measured and known values that characterize the ion and aerosol properties on 29 March 2000. n+ and n– are the concentrations of small ions of positive and negative polarity, respectively; N– is the concentration of negatively charged nanoparticles within the size range 2.8–8.6 nm; No is the concentration of neutral nanoparticles within the same size range. The concentrations presented in a particular column are divided by the number given in the first row of this column. This division is done to achieve similarity with the values presented in the Figure 2 of the main text. All these values, in addition to the values listed in Table S1a, are used as known parameters to estimate the searched free parameters.

LST	n+/100	n–/100	N–/10	No/500
9:00	4,0	3,6	0,9	1,0
9:30	3,9	3,5	1,3	1,5
10:00	3,9	3,5	2,4	3,9
10:30	3,4	3,1	10,0	15,7
11:00	3,1	2,8	14,6	29,7
11:30	3,0	2,8	19,8	31,5
12:00	2,9	2,6	19,0	27,0
12:30	2,8	2,5	17,6	23,5
13:00	2,9	2,6	14,9	15,1
13:30	3,2	2,9	3,1	7,5
14:00	3,2	2,9	5,9	7,0
14:30	3,2	2,9	3,3	4,9
15:00	3,2	2,9	3,2	4,1
15:30	3,1	2,8	4,8	3,5
16:00	3,2	2,9	2,4	2,9
16:30	3,3	3,0	1,4	2,5
17:00	3,4	3,1	1,1	1,7
17:30	3,5	3,2	0,6	1,9

Table S2a. Measured meteorological and background aerosol parameters at the SMEAR II station, Hyytiälä, on 30 March 2000. Column "LST" presents the time, when the particular parameters were measured. "Initial, halftime and final" mark the corresponding points in the simulated time interval. Abbreviation BP marks background aerosol particles larger than 8.6 nm.

Parameter	LST	Value	Unit
Air temperature	13:30	9	Celsius
Air pressure	13:30	991	millibar
Initial average diameter of BP	08:00	60	nm
Halftime average diameter of BP	13:30	48	nm
Final average diameter of BP	19:30	55,0	nm
Initial concentration of BP	08:00	3820	cm^{-3}
Halftime concentration of BP	13:30	3780	cm^{-3}
Final concentration of BP	19:30	3550	cm^{-3}

Table S2b. Measured and known values that characterize the ion and aerosol properties on 30 March 2000. n+ and n– are the concentrations of small ions of positive and negative polarity, respectively; N– is the concentration of negatively charged nanoparticles within the size range 2.8–8.6 nm; No is the concentration of neutral nanoparticles within the same size range. The concentrations presented in a particular column are divided by the number given in the first row of this column. This division is done to achieve similarity with the values presented in the Figure 2 of the main text. All these values, in addition to the values listed in Table S2a, are used as known parameters to estimate the searched free parameters.

LST	n+/100	n–/100	N–/10	No/500
8:30	4,1	3,8	0,1	0,2
9:00	4,3	3,9	0,1	0,2
9:30	4,5	4,1	0,3	0,2
10:00	4,7	4,2	0,7	0,4
10:30	4,7	4,3	2,1	0,8
11:00	4,6	4,2	1,7	0,7
11:30	4,6	4,2	2,8	0,8
12:00	4,9	4,4	2,8	0,8
12:30	5,1	4,7	3,4	1,3
13:00	5,3	4,8	3,8	1,3
13:30	5,1	4,6	2,8	1,4
14:00	4,8	4,4	2,3	1,6
14:30	4,5	4,1	2,9	1,6
15:00	4,0	3,7	2,2	1,6
15:30	4,9	4,4	1,4	0,8
16:00	5,3	4,8	1,2	0,6
16:30	5,2	4,8	1,0	0,6
17:00	5,3	4,9	1,3	1,0
17:30	5,0	4,6	0,7	0,5
18:00	4,7	4,3	0,3	0,4
18:30	4,9	4,4	0,2	0,3
19:00	5,3	4,8	0,1	0,1
19:30	5,4	4,9	0,1	0,1

Table S3a. Measured meteorological and background aerosol parameters at the SMEAR II station, Hyytiälä, on 2 April 2000. Column "LST" presents the time, when the particular parameters were measured. "Initial, halftime and final" mark the corresponding points in the simulated time interval. Abbreviation BP marks background aerosol particles larger than 8.6 nm.

Parameter	LST	Value	Unit
Air temperature	15:00	-0.4	Celsius
Air pressure	15:00	995	millibar
Initial average diameter of BP	10:00	57	nm
Halftime average diameter of BP	15:00	28	nm
Final average diameter of BP	20:00	31,0	nm
Initial concentration of BP	10:00	900	cm^{-3}
Halftime concentration of BP	15:00	1430	cm^{-3}
Final concentration of BP	20:00	4660	cm^{-3}

Table S3b. Measured and known values that characterize the ion and aerosol properties on 2 April 2000. n+ and n– are the concentrations of small ions of positive and negative polarity, respectively; N– is the concentration of negatively charged nanoparticles within the size range 2.8–8.6 nm; No is the concentration of neutral nanoparticles within the same size range. The concentrations presented in a particular column are divided by the number given in the first row of this column. This division is done to achieve similarity with the values presented in the Figure 2 of the main text. All these values, in addition to the values listed in Table S3a, are used as known parameters to estimate the searched free parameters.

LST	n+/100	n–/100	N–/10	No/500
10:30	6,7	6,1	0,9	0,3
11:00	6,5	5,9	1,1	0,6
11:30	6,4	5,9	2,7	0,9
12:00	6,7	6,1	1,1	0,7
12:30	6,9	6,2	2,8	1,8
13:00	6,4	5,8	4,6	3,1
13:30	6,4	5,8	3,8	3,1
14:00	6,3	5,7	5,4	3,4
14:30	6,4	5,8	4,5	3,8
15:00	6,2	5,7	4,1	3,8
15:30	5,9	5,4	5,3	4,7
16:00	6,0	5,4	5,4	4,3
16:30	5,6	5,1	3,1	2,6
17:00	5,8	5,3	2,2	1,9
17:30	5,5	5,0	2,1	1,7
18:00	6,0	5,4	1,6	1,2
18:30	6,1	5,6	0,9	0,6
19:00	6,8	6,2	0,6	0,5
19:30	7,1	6,4	0,4	0,2
20:00	7,4	6,7	0,2	0,1

Table S4a. Measured meteorological and background aerosol parameters at the SMEAR II station, Hyytiälä, on 6 April 2000. Column "LST" presents the time, when the particular parameters were measured. "Initial, halftime and final" mark the corresponding points in the simulated time interval. Abbreviation BP marks background aerosol particles larger than 8.6 nm.

Parameter	LST	Value	Unit
Air temperature	15:00	3.5	Celsius
Air pressure	15:00	987	millibar
Initial average diameter of BP	10:00	40	nm
Halftime average diameter of BP	15:00	47	nm
Final average diameter of BP	20:00	23,0	nm
Initial concentration of BP	10:00	1030	cm^{-3}
Halftime concentration of BP	15:00	610	cm^{-3}
Final concentration of BP	20:00	3300	cm^{-3}

Table S4b. Measured and known values that characterize the ion and aerosol properties on 6 April 2000. n+ and n– are the concentrations of small ions of positive and negative polarity, respectively; N– is the concentration of negatively charged nanoparticles within the size range 2.8–8.6 nm; No is the concentration of neutral nanoparticles within the same size range. The concentrations presented in a particular column are divided by the number given in the first row of this column. This division is done to achieve similarity with the values presented in the Figure 2 of the main text. All these values, in addition to the values listed in Table S4a, are used as known parameters to estimate the searched free parameters.

LST	n+/100	n–/100	N–/10	No/500
10:30	6,3	5,8	0,28	0,37
11:00	6,3	5,8	0,31	0,47
11:30	6,5	5,9	0,42	0,52
12:00	6,4	5,8	0,48	0,86
12:30	6,1	5,6	1,09	1,41
13:00	6,3	5,7	0,66	1,10
13:30	6,3	5,7	0,74	0,96
14:00	6,3	5,7	0,76	0,72
14:30	6,3	5,8	0,45	0,48
15:00	6,3	5,7	0,99	0,89
15:30	6,3	5,8	1,04	1,12
16:00	5,9	5,4	1,53	1,36
16:30	5,7	5,2	2,26	1,92
17:00	5,5	5,0	1,99	1,48
17:30	5,4	4,9	1,15	0,95
18:00	6,2	5,7	0,53	0,66
18:30	6,6	6,0	0,48	0,56
19:00	6,5	5,9	0,46	0,49
19:30	6,5	5,9	0,59	0,37
20:00	7,0	6,4	0,28	0,43

Table S5a. 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. "Initial, halftime and final" mark the corresponding points in the simulated time interval. 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
Halftime 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}
Halftime concentration of BP	11:30	4380	cm^{-3}
Final concentration of BP	16:30	6140	cm^{-3}

Table S5b. Measured and known values that characterize the ion and aerosol properties on 7 April 2000. n+ and n– are the concentrations of small ions of positive and negative polarity, respectively; N– is the concentration of negatively charged nanoparticles within the size range 2.8–8.6 nm; No is the concentration of neutral nanoparticles within the same size range. The concentrations presented in a particular column are divided by the number given in the first row of this column. This division is done to achieve similarity with the values presented in the Figure 2 of the main text. All these values, in addition to the values listed in Table S5a, are used as known parameters to estimate the searched free parameters.

LST	n+/100	n–/100	N–/10	No/500
7:30	8,3	7,6	0,6	0,4
8:00	7,9	7,2	0,4	0,4
8:30	7,8	7,1	2,2	0,6
9:00	7,3	6,6	2,2	1,2
9:30	6,8	6,2	2,2	1,7
10:00	6,5	5,9	3,4	2,6
10:30	6,2	5,6	3,7	2,5
11:00	5,4	4,9	6,1	4,0
11:30	5,6	5,1	7,1	4,8
12:00	5,5	5,0	6,2	3,8
12:30	5,5	5,0	5,9	3,2
13:00	5,3	4,8	3,6	2,1
13:30	5,2	4,7	2,6	1,5
14:00	5,4	4,9	3,3	1,7
14:30	5,3	4,8	2,0	1,4
15:00	5,5	5,0	2,0	1,1
15:30	5,3	4,8	1,9	0,9
16:00	4,8	4,4	1,0	0,5
16:30	4,8	4,3	0,6	0,4

Table S6a. Measured meteorological and background aerosol parameters at the SMEAR II station, Hyytiälä, on 8 April 2000. Column "LST" presents the time, when the particular parameters were measured. "Initial, halftime and final" mark the corresponding points in the simulated time interval. Abbreviation BP marks background aerosol particles larger than 8.6 nm.

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
Halftime 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}
Halftime concentration of BP	11:00	5000	cm^{-3}
Final concentration of BP	14:30	15300	cm^{-3}

Table S6b. Measured and known values that characterize the ion and aerosol properties on 8 April 2000. n+ and n– are the concentrations of small ions of positive and negative polarity, respectively; N– is the concentration of negatively charged nanoparticles within the size range 2.8–8.6 nm; No is the concentration of neutral nanoparticles within the same size range. The concentrations presented in a particular column are divided by the number given in the first row of this column. This division is done to achieve similarity with the values presented in the Figure 2 of the main text. All these values, in addition to the values listed in Table S6a, are used as known parameters to estimate the searched free parameters.

LST	n+/100	n–/100	N–/10	No/500
8:30	6,7	6,1	1,5	0,3
9:00	6,6	6,0	1,0	0,4
9:30	6,1	5,6	2,5	1,0
10:00	5,8	5,2	3,1	1,0
10:30	5,4	4,9	7,9	2,9
11:00	5,1	4,6	7,5	2,7
11:30	4,5	4,1	6,1	2,1
12:00	4,4	4,0	7,4	3,9
12:30	4,1	3,8	8,8	3,4
13:00	3,9	3,6	5,2	1,7
13:30	4,0	3,7	5,4	2,5
14:00	3,3	3,0	2,0	0,8
14:30	3,6	3,2	2,0	1,5

Table S7a. Measured meteorological and background aerosol parameters at the SMEAR II station, Hyytiälä, on 9 April 2000. Column "LST" presents the time, when the particular parameters were measured. "Initial, halftime and final" mark the corresponding points in the simulated time interval. Abbreviation BP marks background aerosol particles larger than 8.6 nm.

Parameter	LST	Value	Unit
Air temperature	11:30	5	Celsius
Air pressure	11:30	1003	millibar
Initial average diameter of BP	07:30	59,3	nm
Halftime average diameter of BP	11:30	44	nm
Final average diameter of BP	16:00	33,6	nm
Initial concentration of BP	07:30	2680	cm^{-3}
Halftime concentration of BP	11:30	3650	cm^{-3}
Final concentration of BP	16:00	7990	cm^{-3}

Table S7b. Measured and known values that characterize the ion and aerosol properties on 9 April 2000. n+ and n– are the concentrations of small ions of positive and negative polarity, respectively; N– is the concentration of negatively charged nanoparticles within the size range 2.8–8.6 nm; No is the concentration of neutral nanoparticles within the same size range. The concentrations presented in a particular column are divided by the number given in the first row of this column. This division is done to achieve similarity with the values presented in the Figure 2 of the main text. All these values, in addition to the values listed in Table S7a, are used as known parameters to estimate the searched free parameters.

LST	n+/100	n–/100	N–/10	No/500
8:00	5,4	4,9	0,04	0,03
8:30	5,4	4,9	0,30	0,32
9:00	5,5	5,0	0,47	0,42
9:30	5,2	4,8	0,84	0,47
10:00	4,7	4,3	1,20	0,52
10:30	4,6	4,2	3,31	1,39
11:00	4,3	3,9	5,40	3,52
11:30	4,4	4,0	2,82	1,64
12:00	5,0	4,6	1,05	0,31
12:30	4,9	4,4	1,28	0,41
13:00	4,7	4,2	0,99	0,35
13:30	4,8	4,4	0,54	0,38
14:00	4,9	4,4	0,68	0,39
14:30	4,4	4,0	0,36	0,22
15:00	4,4	4,0	0,38	0,21
15:30	4,1	3,8	0,33	0,36
16:00	4,1	3,7	0,28	0,22

Table S8. Measured and simulated concentrations of nanoparticles (in cm^{-3}) and the estimated charged fractions of nanoparticles (%) at the SMEAR II station, Hyytiälä, on 30 March 2000. Column "LST" presents LST time. "N–, meas" presents the measured concentrations of negative nanoparticles. "N–, sim" and "N+, sim" contain the simulated concentrations of negative and positive nanoparticles, respectively. "No, App. S1" is the concentrations of neutral nanoparticles that calculated using the measured data and the algorithm presented in Appendix S1. "No, sim" is the concentrations of neutral nanoparticles, obtained by simulations. The size range of abovementioned nanoparticles is 2.8–8.6 nm. "Charged %, meas" represents the charged fraction of negative nanoparticles, calculated from measured data and assuming that N– = N+. "Charged %, sim" represents the charged fraction of negative nanoparticles, calculated from simulated data. Columns "…(1)" contain the data at all time points, columns "…(2)" contain only the data, where all "N–" and "No" are substantially above zero (at least 5% from the maximal value).

LST	N–, meas	No, App. S1	Charged %, meas(1)	Charged %, meas(2)	N–, sim	N+, sim	No, sim	Charged %, sim(1)	Charged %, sim(2)
8:30	0,7	84	0,8		0,0	0,0	0		
9:00	1,1	110	1,0		1,3	1,3	5	17,1	
9:30	2,9	107	2,6		4,6	4,6	40	9,3	
10:00	7,4	175	3,9	3,9	10,1	10,0	135	6,5	6,5
10:30	21,4	408	4,7	4,7	17,1	17,0	290	5,3	5,3
11:00	17,0	344	4,5	4,5	22,9	22,7	465	4,5	4,5
11:30	28,3	422	5,9	5,9	27,3	26,9	590	4,2	4,2
12:00	27,9	406	6,0	6,0	29,8	29,4	660	4,1	4,1
12:30	34,4	636	4,9	4,9	31,2	30,8	700	4,1	4,1
13:00	37,6	653	5,2	5,2	31,4	31,0	730	4,0	4,0
13:30	28,1	718	3,6	3,6	30,6	30,2	725	3,9	3,9
14:00	23,4	796	2,8	2,8	28,6	28,2	685	3,9	3,9
14:30	29,1	811	3,3	3,3	25,8	25,5	625	3,8	3,8
15:00	22,4	783	2,7	2,7	22,7	22,5	560	3,8	3,8
15:30	13,9	385	3,4	3,4	19,5	19,3	485	3,7	3,7
16:00	11,8	286	3,8	3,8	16,3	16,1	410	3,7	3,7
16:30	9,9	284	3,3	3,3	13,0	12,9	330	3,7	3,7
17:00	13,4	476	2,7	2,7	10,0	9,9	260	3,6	3,6
17:30	6,7	273	2,3	2,3	7,2	7,1	190	3,5	3,5
18:00	3,2	185	1,7	1,7	4,7	4,7	130	3,4	3,4
18:30	2,2	130	1,6	1,6	2,7	2,6	80	3,2	3,2
19:00	1,2	67	1,7		1,2	1,2	40	2,8	
19:30	0,9	37	2,3		0,4	0,4	10	3,7	
Average			3.3	3.7				4.8	4.0

FIGURE CAPTIONS

Fig S1. Flowchart of the estimation algorithm. The marks used in the Figure are as follows. p_i are the values of physical input parameters, 61 values in total (i = 1…61). In principle all these values can be the ones that are to be estimated by the estimator. Actually (in the present study) we estimate only 39 values, other parameters have certain constant values valid within all the estimation process. The constant values are distinguished by the value of the corresponding increment, Δ_i. In case a particular increment has initial value, equal to zero, the corresponding parameter is considered constant from the beginning of the estimation process. In case the value of a particular increment becomes zero within the estimation process, the estimation of the corresponding parameter stops and henceforth this parameter is considered constant, equal to the value that this parameter obtained within the estimation process. For the changeable parameters the initial value of Δ_i is usually 15%, but this value can automatically decrease within the estimation process. A particular increment Δ_i determines the variation that is applied to the corresponding parameter within one single estimation step within the estimation loop. Within the estimation loop the variations can accumulate and in summary the applied variations can obtain large values. In the flowchart a particular estimation step starts from the box that contains text "Repeat for all input parameters…" and ends by the box that contains text "If $SUM_c < 0.99*SUM_0$ …". This estimation step is repeated until this condition becomes invalid.

p_k are also the values of physical input parameters, but the series { p_k } contains only the values of these parameters that are accompanied by the increments that are not equal to zero, $\Delta_k \neq 0$. The number of the values in the series { p_k } can be up to 61, but in the present study the initial number of the values is 39 (we estimate only 39 parameters) and within the estimation process this value gradually decreases, correspondingly to the values of the increments Δ_k that can gradually become equal to zero when some parameter is automatically excluded from further estimation.

The four boxes that begin with the box that contains text "If $\Delta_k > 0$, set parameter p_k …" and are surrounded by dashed lines concretize certain operations described in the previous larger box. For example, the box with text "If $\Delta_k > 0$, save the modified vector of parameters p_i…" means that only these vectors are saved or kept (only these vectors will be within the J new input vectors).

OUT_j are the tables that contain simulated time evolution of the selected parameters, the tables are generated as a result of all individual simulations. The total number of these tables (j = 1…J) is equal to the number of unique combinations of input parameters (the number of new modified input vectors) that are introduced to the burst simulator within a particular estimation step. Examples of such tables are the Tables S1b – S7b (these tables are just examples, the actual content of the tables depends on the input parameters, introduced to the burst simulator). Notation $OUT_{j,m,n}$ refers one particular value within the table OUT_j. When to look at an example, e.g. Table S7b, m can be considered the row number and n can be considered the column number where this particular value is located, e.g. $OUT_{S7b,3,4}$ =0,3. Notation $REF_{m,n}$ refers an analogical value within the table REF, whereas OUT_j and REF have exactly same shape. OUT_j contain the values, simulated by burst simulator and REF contain the reference values. In some measure the situation can be interpreted as the estimator looks for the table OUT_j that is closest to the corresponding table REF. When to look at an example, Table S7b can be considered reference table for that particular case (actually, the Tables S1b – S7b are just the reference tables used in this study, one reference table is valid

for one particular case or for one particular NPF event). The tables OUT_c are similar to the tables OUT_j, but the tables OUT_j are used within the first stage of an estimation step, the tables OUT_c are used within the second stage of an estimation step.

The number of the combinations of the five input vectors (31) results from the general rule that determines how the combinations should be computed. In case we have five values (1, 2, 3, 4, 5), the possible unique combinations are 1, 2, 3, 4, 5, 12, 13, 14, 15, 23, 24, 25, 34, 35, 45, 123, 124, 125, 134, 135, 145, 234, 235, 245, 345, 1234, 1235, 1245, 1345, 2345 and 12345. In our estimator a particular number (e.g., 1) means a particular input vector (one from the abovementioned five vectors) and the occurrence of this particular number in a particular combination means that the modifications that are represented in this particular input vector are taken into account (e.g., 123 means that this combination contains all the modifications that are represented in the vectors 1, 2, and 3, but does not contain the modifications that are represented in vectors 4 and 5).

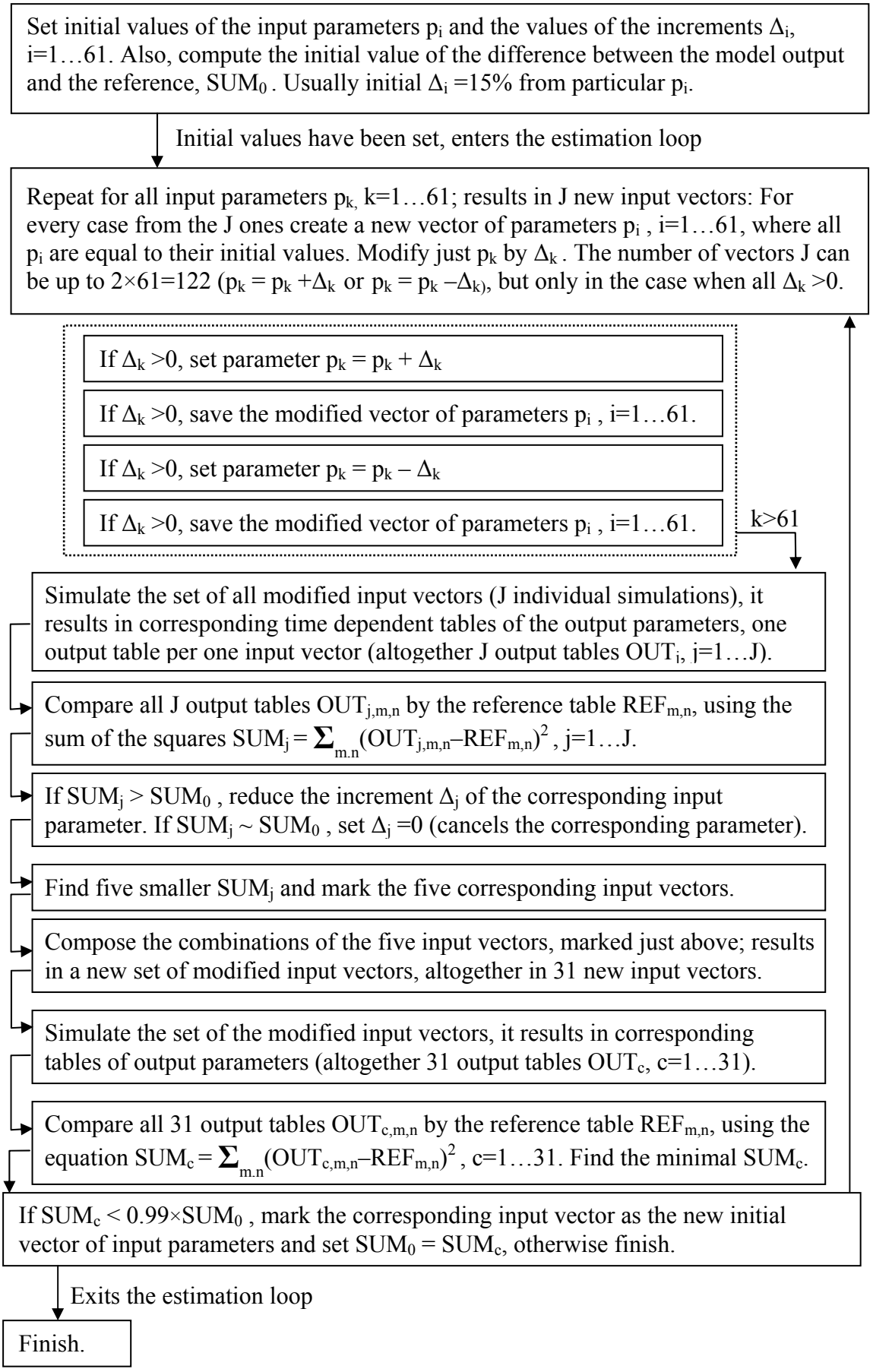
Set initial values of the input parameters p_i and the values of the increments Δ_i, i=1…61. Also, compute the initial value of the difference between the model output and the reference, SUM_0 . Usually initial Δ_i =15% from particular p_i.
Initial values have been set, enters the estimation loop
Repeat for all input parameters p_k, k=1…61; results in J new input vectors: For every case from the J ones create a new vector of parameters p_i , i=1…61, where all p_i are equal to their initial values. Modify just p_k by Δ_k . The number of vectors J can be up to 2×61=122 ($p_k = p_k + \Delta_k$ or $p_k = p_k - \Delta_k$), but only in the case when all Δ_k >0.
If Δ_k >0, set parameter $p_k = p_k + \Delta_k$
If Δ_k >0, save the modified vector of parameters p_i , i=1…61.
If Δ_k >0, set parameter $p_k = p_k - \Delta_k$
If Δ_k >0, save the modified vector of parameters p_i , i=1…61.
k>61
Simulate the set of all modified input vectors (J individual simulations), it results in corresponding time dependent tables of the output parameters, one output table per one input vector (altogether J output tables OUT_j, j=1…J).
Compare all J output tables $OUT_{j,m,n}$ by the reference table $REF_{m,n}$, using the sum of the squares $SUM_j = \sum_{m.n}(OUT_{j,m,n} - REF_{m,n})^2$, j=1…J.
If $SUM_j > SUM_0$, reduce the increment Δ_j of the corresponding input parameter. If $SUM_j \sim SUM_0$, set Δ_j =0 (cancels the corresponding parameter).
Find five smaller SUM_j and mark the five corresponding input vectors.
Compose the combinations of the five input vectors, marked just above; results in a new set of modified input vectors, altogether in 31 new input vectors.
Simulate the set of the modified input vectors, it results in corresponding tables of output parameters (altogether 31 output tables OUT_c, c=1…31).
Compare all 31 output tables $OUT_{c,m,n}$ by the reference table $REF_{m,n}$, using the equation $SUM_c = \sum_{m.n}(OUT_{c,m,n} - REF_{m,n})^2$, c=1…31. Find the minimal SUM_c.
If $SUM_c < 0.99 \times SUM_0$, mark the corresponding input vector as the new initial vector of input parameters and set $SUM_0 = SUM_c$, otherwise finish.
Exits the estimation loop
Finish.

Fig. S1.