

1 Ion – particle interactions during particle formation and 2 growth at a coniferous forest site in central Europe

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12 13 **Abstract**

14 In this work, we examined the interaction of ions and neutral particles during atmospheric
15 new particle formation (NPF) events. The analysis is based on simultaneous field
16 measurements of atmospheric ions and total particles using a neutral cluster and air ion
17 spectrometer (NAIS) across the diameter range 2 - 25 nm. The “Waldstein” research site is
18 located in a spruce forest in NE Bavaria, Southern Germany, known for enhanced radon
19 concentrations, presumably leading to elevated ionization rates. Our observations show that
20 the occurrence of the ion nucleation mode preceded that of the total particle nucleation mode
21 during all analysed NPF events. The time difference between the appearance of 2 nm ions and
22 2 nm total particles was typically about 20 to 30 minutes. A cross correlation analysis showed
23 a rapid decrease of the time difference between the ion and total modes during the growth
24 process. Eventually, this time delay vanished when both ions and total particles did grow to
25 larger diameters. Considering the growth rates of ions and total particles separately, total
26 particles exhibited enhanced growth rates at diameters below 15 nm. This observation cannot
27 be explained by condensation or coagulation, because these processes would act more
28 efficiently on charged particles compared to neutral particles. To explain our observations, we

1 propose a mechanism including recombination and attachment of continuously present cluster
2 ions with the ion nucleation mode and the neutral nucleation mode, respectively.

3

4 **1 Introduction**

5 Tropospheric new particle formation (NPF) is a worldwide phenomenon (Kulmala et al.,
6 2004a; Kulmala and Kerminen, 2008) contributing to the global particle number and total
7 amount of cloud condensation nuclei (Makkonen et al., 2012, Merikanto et al., 2009;
8 Spracklen et al., 2006;). The first step leading to NPF is thought to be the formation of stable
9 clusters from precursor gas phase components as sulfuric acid, amines, ammonia and organic
10 vapors (Almeida et al. 2013; Kulmala et al., 2013; Schobesberger et al., 2013). The formation
11 of stable clusters happens in the mobility diameter (D_m) range between 1 to 2 nm. Once
12 formed, the stable clusters are activated and experience rapid growth (Kulmala et al., 2013).
13 Atmospheric ions are very likely to play a considerable role in atmospheric nucleation
14 processes, as ions reduce the critical cluster size and facilitate cluster activation (e.g. Enghoff
15 and Svensmark, 2008; Winkler et al., 2008; Yue and Chan, 1979). In fact, comprehensive
16 field measurements of NPF events at different locations in Europe showed an earlier
17 formation of charged particles compared to total particles (neutral + charged particles;
18 Manninen et al., 2010). Furthermore, the charging state of aerosol particles during NPF was
19 observed to be frequently overcharged (Gagné et al., 2010; Iida et al., 2006; Laakso et al.,
20 2007). The ratio of charged particle concentrations to neutral particle concentrations in a
21 defined diameter interval is defined as the charged fraction. In a bipolar ion environment, the
22 size-dependent charged fraction of an aerosol will eventually reach an equilibrium charging
23 state due to ion-particle interactions (Fuchs, 1963; Wiedensohler, 1988). When the charged
24 fraction is elevated in comparison to the equilibrium charged fraction, an aerosol is defined to
25 be in an overcharged charging state.

26 When ions are involved in the nucleation process, two terms are usually used: ion induced
27 nucleation (IIN; e.g. Manninen et al. (2010)) and ion mediated nucleation (IMN; e.g. Yu and
28 Turco (2000)). IIN denotes the formation of particles from small ionic clusters, preserving the
29 charge during growth process. Additionally, when interactions of ions and particles are taken
30 into account the term IMN is used. Hence, IMN includes IIN and does also consider
31 interactions among ions and particles, like recombination and attachment.

1 Yu (2006) developed a detailed model to simulate the IMN process. Results from this model
2 point towards the dominant role of ions in NPF, especially, when the actual aerosol charged
3 fraction is elevated in comparison to the equilibrium charging state (Yu and Turco, 2011). On
4 the other hand, when comparing formation rates of charged particles to total particle
5 formation rates, only a small fraction (usually less than 10 %) of the particle formation can be
6 attributed to IIN (Manninen et al., 2009a; 2010). However, this approach does not account for
7 ion-ion and ion-particle interactions, which are potentially contributing largely to NPF (Yu
8 and Turco, 2011). Only recently, Kulmala et al. (2013) and Kontkanen et al. (2013) published
9 results of field measurements with a sophisticated set of instruments, covering the size range
10 where the very first steps of NPF take place. From their data and theoretical calculations of
11 ion-ion recombination, Kulmala et al. (2013) and Kontkanen et al. (2013) concluded that pure
12 neutral nucleation processes dominate over IMN.

13 Atmospheric ions are generally classified according to their electric mobility diameter D_m into
14 three classes: (1) small ions or cluster ions ($D_m < 1.6$ nm), (2) intermediate ions (1.6 nm $< D_m$
15 < 7.4 nm) and (3) large ions ($D_m > 7.4$ nm) (e.g. Hirsikko et al., 2011). Small atmospheric
16 ions are always present in the atmosphere, being mainly generated by radioactive decay and
17 cosmic radiation. The total concentration of small ions varies spatially and temporally,
18 depending on ion sources and sinks (Hirsikko et al. (2011) and references therein). Elevated
19 concentrations of intermediate and large ions are usually only present during (1) NPF events,
20 where small ions grow due to condensation of precursor gases, (2) snow fall associated with
21 high wind speeds, where friction processes between the snowflakes are thought to be a source
22 for intermediate ions (Virkkula et al., 2007), and (3) rain, where the splashing of rain droplets
23 generates intermediate ions due to the balloelectric effect (Tammet et al., 2009).

24 Only during the last decade, appropriate instrumentation became available to measure neutral
25 and charged cluster size distributions down to diameters relevant for NPF (Kulmala et al.,
26 2012). One instrument capable of measuring ions down to D_m of about 0.8 nm and neutral
27 particles down to 2 nm is the neutral cluster and air ion spectrometer (NAIS) (Manninen et al.,
28 2009b; 2011; Mirme and Mirme, 2013). In this paper, we present measurements performed
29 with the NAIS during NPF. A new approach to evaluate the data is proposed to elucidate the
30 interactions of ions and neutral particles in the formation and growth of atmospheric particles.

31

1 **2 Measurements and data analysis**

2 **2.1 Measurement setup**

3 New particle formation (NPF) events were observed from 17 June to 18 August, 2012 at the
4 “Waldstein” ecosystem research site in the Fichtelgebirge mountain range, NE Bavaria,
5 Southern Germany. The measurements were carried out in a coniferous forest (50°08'35'' N,
6 11°51'49'' E, 776 m above sea level) dominated by Norway spruce. NPF was measured by
7 means of a neutral cluster and air ion spectrometer (S/N NAIS15) (Airel Ltd., Tartu, Estonia)
8 and a mobility particle size spectrometer (reference system of TROPOS, Leipzig, Germany;
9 Wiedensohler et al., 2012).

10 The NAIS is capable of measuring neutral particles in the diameter range from about 2 nm to
11 42 nm and atmospheric ions in the range of 0.8 nm to 42 nm (Manninen et al., 2011). The
12 NAIS is composed of two cylindrical differential mobility analyzers (DMA), each with a
13 sample flow of 30 standard liters per minute (SLM) and a sheath flow of 60 SLM. Each DMA
14 is equipped with 21 electrometers for simultaneous detection of ions. Positive and negative
15 ions are analyzed separately in a positive and a negative DMA, respectively. The NAIS can be
16 used in different operating modes. In the particle mode, clusters are charged by corona
17 discharge prior to the mobility analysis in one of the DMAs. During ion measurement mode
18 the sample is directed to the DMAs without any prior treatment. The offset mode is used for
19 detection of the electrometer background noise level. To do this, charging to opposite polarity
20 and an electric filter is activated inhibiting the introduction of ions to the DMAs. During the
21 whole campaign the NAIS was operated alternatingly with these three modes: offset mode,
22 ion mode and particle mode. The cycle time of the consecutive modes was 200 seconds, with
23 the particle mode set to 66 seconds, the ion mode set to 67 seconds and the offset mode set to
24 67 seconds. Therefore, the overall temporal resolution of the NAIS was 200 seconds.

25 In particle mode, the recorded number size distribution is inverted by the instrument software,
26 assuming the Fuchs-charge equilibrium of the sample prior to charging and that all classified
27 particles are singly charged. However, if the particle population is not in charge equilibrium
28 but either overcharged or undercharged, the NAIS will overestimate or underestimate the total
29 particle concentrations, respectively (Kulmala et al., 2012). During NPF the charging state of
30 aerosol particles was observed to be frequently overcharged (Gagné et al., 2010; Iida et al.,
31 2006; Laakso et al., 2007). Additionally, an overestimation of the total particle concentration

1 by a factor of 2-3 is a general characteristic of NAIS instruments, as was shown by an
2 intercomparison of several NAIS instruments by Gagné et al., (2011). Therefore, total particle
3 concentrations in this study are very likely to be overestimated. In the ion mode, no charging
4 of the sample is performed and the DMAs sample the naturally charged clusters. The NAIS is
5 described in more detail by Manninen et al. (2009b) and Mirme and Mirme (2013).

6 The particle number size distributions measured with the mobility particle size spectrometer
7 cover a diameter size range from 10 nm to 680 nm with a temporal resolution of 5 minutes. It
8 was operated with a closed loop sheath flow of 5 SLM and a sample flow of 1 SLM. More
9 details about the mobility particle size spectrometer are described in Wiedensohler et al.
10 (2012; cf. Fig. 1). Both instruments were located in a container on a clearing in the forest with
11 the inlets pointing towards east, at a height of 2 m above ground. Additionally, meteorological
12 parameters including ozone concentration, wind speed, wind direction, temperature, relative
13 humidity as well direct and diffuse solar radiation were measured at the forest clearing.

14 To obtain robust information about the processes governing NPF from measurements at a
15 fixed location, the analyzed nucleation events have to be of regional character, and occur in a
16 generally homogenous air mass. The homogeneity of air masses was assessed by considering
17 the following parameters: Wind direction, wind speed, ozone concentration, relative humidity
18 and particle concentration in the diameter range from 4 to 10 nm. Only when wind speeds
19 varied less than 0.5 m s^{-1} and wind directions varied less than 60° prior and during NPF, and
20 all other parameters showed a continuous and consistent progression, the air mass was judged
21 to be homogeneous.

22 The focus of this study is to determine ion interactions during NPF measured with the NAIS.
23 Hence, the data of the mobility particle size spectrometer was mainly considered for
24 calculations of ion and total particle sink rates. For this purpose, the NAIS particle data were
25 merged with this data by means of a linearly weighted merging algorithm in the overlapping
26 region of both instruments between 15 and 27 nm. The mobility particle size spectrometer
27 was measuring with a 5 minute temporal resolution and its size bins were different from the
28 NAIS size bins. Both the size bins and the time resolution were interpolated to match the
29 NAIS time resolution and size bins. The resultant particle number size distribution between
30 2 nm and 680 nm was used for calculating the sink rates for ions and total particles according
31 to Hörrak et al. (2008), Kulmala et al. (2012) and Tammet and Kulmala (2005).

32

1 2.2 Interactions of ions and neutral particles

2 The major interactions of ions and neutral particles among themselves and with the
3 background aerosol particle population are (1) coagulation of neutral particles, (2) attachment
4 of ions to neutral particles and (3) recombination of ions with ions of opposing polarity. The
5 magnitude of these interactions can be calculated theoretically as corresponding coefficients
6 (see appendix for the formulations).

7 Coagulation (1) is an important sink for freshly nucleated particles and a factor enhancing the
8 particle growth rate (GR) during NPF events (Kulmala et al., 2004b). To determine the size-
9 dependent coagulation coefficient K_{ij} , an approximation from Tammet and Kulmala (2005)
10 was used (cf. Eqs. A1 and A2). The theoretical approach for K_{ij} is valid for the interaction of
11 neutral particles and clusters of all diameters i and j .

12 The ion aerosol attachment (2) is described by the attachment coefficient β for the interaction
13 of small air ions with neutral particles. β is commonly assumed constant ($1 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) when
14 determining ion formation rates, where the attachment of small ions to neutral particles of a
15 large diameter is considered a source for ions of the same diameter (Hirsikko et al., 2011;
16 Kulmala et al., 2012; Manninen et al., 2010). However, this size-independent approach is only
17 an approximation. In particular, when the diameter i of neutral particles is greater than 10 nm,
18 a constant value is inaccurate (cf. green solid line in Fig. 1). Therefore, when calculating ion
19 sinks, the size dependence of β has to be taken into account. The size dependent β_{ij} varies by
20 three orders of magnitude, when the interactions of small ions of size j with neutral particles
21 of size i are considered (cf. solid green line in Fig. 1; Hoppel and Frick, 1990; Hörrak et al.,
22 2008; Tammet and Kulmala, 2005). For this study, we determined β_{ij} by applying a
23 formulation by Hörrak et al. (2008), which is an approximation of the tabulated results by
24 Hoppel and Frick (1990) (cf. Eqs. A3 and A4). Since intermediate and large ions also have a
25 slightly enhanced attachment probability compared to pure neutral coagulation (cf. Fig. 1,
26 dashed lines), we extrapolated β_{ij} for all measured ion size ranges, still using the formulation
27 by Hörrak et al. (2008).

28 In principle, the ion-ion recombination (3) can also be described by the attachment
29 coefficient, assuming the interaction of clusters with opposite charges. Usually, the
30 recombination coefficient is denoted as α and assumed to be constant ($1.6 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$) when
31 the interaction among small ions is considered (Hoppel and Frick, 1990; Kulmala et al., 2013;

1 Tammet and Kulmala, 2005). Considering the case of cluster ions of diameter j interacting
2 with oppositely charged clusters of a similar diameter k , β_{jk} should be comparable to the
3 constant value of α (Hoppel and Frick, 1986). In fact, β_{jk} for ions with $j = 1.5$ nm interacting
4 with oppositely charged ions with $k = 1.5$ nm, as used in this study, is $1.3 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ (solid
5 orange line in Fig. 1). Therefore, β_{jk} for the interaction of oppositely charged clusters in the
6 sizes class j and k , i.e. the size-dependent recombination coefficient, will be denoted as α_{jk} in
7 the following (Eq. A5).

8 The theory for ion attachment and recombination was developed to calculate the attachment
9 of small ions to larger particles or ions, in order to theoretically assess the particle charge
10 distribution in a bipolar ion environment (Hoppel and Frick, 1986; 1990; Reischl et al., 1996).
11 The interaction of intermediate and large ions with even larger neutral or charged particles
12 was not the aim of these studies. Nevertheless, the sinks and sources for all ion sizes have to
13 be taken into account when analyzing ion interactions in NPF. Therefore, we chose to use the
14 approximated theory from Hörrak et al. (2008) to obtain a first order approximation of the
15 coefficients governing the behavior of larger ions, and to apply the calculations also for larger
16 diameters. A validation of this approach is given by comparing the size dependence of β and α
17 to K . In Fig. 1, all three coefficients are depicted for aerosols of two different diameters (1.5
18 and 10 nm). As electrical effects will enhance the probability of an encounter of two particles,
19 K is the lower limit for the three considered interactions. When small ions (1.5 nm) and small
20 neutral particles interact with each other (green solid line in Fig. 1), the electrical effect can
21 enhance the collision probability by more than one order of magnitude. Considering the
22 interaction of oppositely charged ions, the enhancement can be greater than three orders of
23 magnitude (orange solid line in Fig. 1). The largest differences are found for interactions of
24 small particles or ions. However, when small ions interact with larger particles or ions, α and
25 β approach K , indicating a smaller influence of the charge on the collision probability. A
26 similar pattern can be seen when considering the interaction of large ions with larger aerosol
27 particles (dashed lines in Fig. 1). For the interaction of particles or ions with a diameter of
28 10 nm, α and β decrease about 1-2 orders of magnitude while K is not that strongly affected.
29 The difference among the three coefficients is less pronounced, pointing towards a smaller
30 influence of the charge on collision probabilities when larger ions and particles are
31 considered.

32

1 2.3 Ion-ion recombination

2 Knowing the recombination coefficient α_{jk} and the number concentration of ions of both
3 polarities, a theoretical number size distribution of neutral particles from ion-ion
4 recombination can be deduced. Kontkanen et al. (2013) and Kulmala et al. (2013) proposed a
5 method to calculate the number size distribution resulting from recombination. Both authors
6 used a constant value of $1.6 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ for α . This is justified since only recombination of
7 charged clusters below 2.1 nm in diameter was considered. However, we use the size-
8 dependent α_{jk} for our approach as the recombination of charged clusters up to 42 nm is
9 considered. Furthermore, Kulmala et al. (2013) used a very simple balance equation, by
10 assuming recombination as the only source of neutral clusters and coagulations as the only
11 sink. Similar to Kontkanen et al. (2013), our analysis includes additional sinks and source
12 terms. The sources are given by the recombination of positive and negative ions contributing
13 to size class i as well as the growth of recombined neutral particles into size class i . The sinks
14 include (1) the coagulation sink ($CoagS_i$; cf. Eq. A6) describing the loss of the recombined
15 neutral particles to the background neutral particles, (2) the charging sink ($CharS_i^{\pm}$; cf. Eq.
16 A7) defining the number of recombined neutral particles in size i being charged either
17 positively or negatively by the present ions (Hörrak et al., 2008), and (3) the growth sink,
18 describing the growth of recombined neutral particles out of the size class i . The balance
19 equation for recombination is therefore:

20

$$21 \frac{dN_i^{rec}}{dt} = \sum_{jk} r_{jk} \alpha_{jk} N_j^+ N_k^- + N_{i-1}^{rec} \frac{GR_{i-1}}{\Delta Dp} - N_i^{rec} \left(CoagS_i + CharS_i^+ + CharS_i^- + \frac{GR_i}{\Delta Dp} \right), \quad (1)$$

22

23 where, N_i^{rec} is the number concentration of recombined neutral particles in size class i and
24 r_{jk} is a coefficient allocating the recombined neutral particles to size class i . $\frac{GR_i}{\Delta Dp}$ is the neutral
25 growth rate normalized by the size bin width and N_j^+ and N_k^- are the positive and negative ion
26 number concentrations, respectively. Assuming steady state conditions, Eq. 1 provides the
27 number of recombined neutral particles for each size class i . Breakup of the formed clusters as
28 proposed by Kontkanen et al. (2013) and Kulmala et al. (2013) is not taken into account in
29 our formulation. Since the concentration of recombination products did never reach the

1 measured neutral cluster concentration, making the determination of a breakup term
2 impossible.

3 The key parameter governing the concentration of small ions in the atmosphere is the
4 ionization rate Q . For our site, Q was calculated by means of a simplified ion equilibrium
5 equation, assuming steady-state equilibrium (Hoppel and Frick, 1986). This equation assumes
6 the ion production rate to be a function of two ion sink terms, the recombination and the
7 attachment of ions to the present background aerosol (cf. Eq. A8).

8

9 **2.4 Formation- and growth rate**

10 The formation rate J describes the flux of particles or ions into a defined size interval. J was
11 calculated for every size class using Eqs. 9 and 10 from Kulmala et al. (2012).

12 The growth rates were also deduced for every size class, this was done separately for total
13 particles (GR_t) as well as positive (GR_{pos}) and negative ions (GR_{neg}). Growth rates were
14 determined using the maximum concentration method described in detail in section 6A by
15 Kulmala et al. (2012). In order to determine the point in time of the maximum concentration
16 (black filled circles in Fig. 2), we applied a least square polynomial smoothing filter (Savitzky
17 and Golay, 1964) to each of the NAIS size classes. Further smoothing of the determined times
18 of maximum concentration resulted in smooth size dependent growth rates (black curves in
19 Fig. 2). The determination of GRs from particle/ion measurements in the troposphere are
20 always associated with uncertainties (Yli-Juuti et al., 2011) as the growth of a particle
21 population is a dynamic process with several influencing factors. Therefore, the result of a GR
22 analysis from field measurements will always only result in an approximation of the true GR.
23 Besides, as the probability of particles carrying multiple charges in the NAIS increases with
24 particle diameter, the measured number size distribution for larger sizes is less reliable.
25 However, the growth rates for particles smaller than 20 nm in diameter give reasonable
26 results. For ion/particle diameters above 20 nm, the applied method results in an
27 overestimation of the growth rates (cf. Fig. 2). By comparing concentrations as well as growth
28 rates of total particles (Fig. 2 a) and neutral particles (Fig. 2 b), it becomes evident that neutral
29 and total particles exhibit equivalent values. Therefore, data from the NAIS's total particle
30 measurements are used to describe neutral particle characteristics in the following. As the
31 same procedure was applied to all ion and particle measurements, the determined growth rates

1 are well comparable. Further, a correction for self-coagulation of the growing mode was
2 applied to obtain the rates for pure condensational growth (Leppä et al., 2011).

3

4 **3 Results**

5 **3.1 General event characteristics**

6 Simultaneous measurements of neutral and charged clusters and particles at the “Waldstein”
7 ecosystem research site from 17 June to 18 August 2012 showed a frequent occurrence of
8 new particle formation events. Typically, the events occurred during sunny morning hours
9 while wind directions from the east prevailed. However, several events did also occur in the
10 afternoons and when wind directions were not from the east. A total number of 17 NPF events
11 (28 % of measurement period) were observed, while 29 days (47 %) could not be defined as
12 clear events but did still show particle formation. Non-event days were less frequent with only
13 15 out of 61 days. Since the measurements were taken at a fixed location, a reliable evaluation
14 of the patterns governing the formation and growth of particles were only possible in
15 homogeneous air masses. After careful evaluation for homogeneous air masses as described
16 above, a total of 8 events were chosen for detailed analysis. Fig. 2 shows a typical NPF event.
17 Growth rates of those 8 days compare well to prior observations, reporting growth rates in the
18 range from 2.2 to 5.7 nm h⁻¹ at the same location (Held et al., 2004). For particles in diameter
19 range 2 – 3 nm median total particle growth rates (GR_t), negative (GR_{neg}) and positive growth
20 rates (GR_{pos}) were found to be 4.1 nm h⁻¹, 2.4 nm h⁻¹ and 2.8 nm h⁻¹, respectively. Median
21 formation rates *J* for 2-3 nm particles were in the order of 3.5 cm⁻³ s⁻¹, 0.015 cm⁻³ s⁻¹ and 0.02
22 cm⁻³ s⁻¹ for total, negative and positive particles, respectively.

23

24 **3.2 Ion concentrations and ionization rates at “Waldstein”**

25 The “Waldstein” site is located in the Fichtelgebirge mountain range, NE Bavaria. The
26 Fichtelgebirge is known for its enhanced background radioactive radiation levels. In
27 particular, radon is elevated, reaching soil gas activity concentrations of up to 4000 kBq m⁻³
28 (Kemski et al., 2001; Lüers et al., 2007). As the primary sources for atmospheric ions are
29 radon decay, gamma radiation and cosmic radiation (Hirsikko et al., 2011), ion concentrations
30 and ionization rates *Q* are expected to be elevated at the “Waldstein” site. The measurements

1 with the NAIS in summer 2012 showed median concentrations of positive and negative
2 cluster ions on NPF event days of 339 and 148 cm^{-3} , respectively (cf. Tab. 1). The cluster ion
3 concentrations show a clear diurnal variation both on NPF event days and non-event days
4 (Fig. 3). Lüers et al. (2007) conducted radon measurements at the “Waldstein” site and found
5 similar diurnal patterns, hinting towards radon as the major ionization source. Furthermore,
6 our measurements show that cluster ion concentrations are slightly enhanced on NPF events
7 days (Tab. 1). Nevertheless, the concentrations seem quite low compared to values measured
8 at various locations around the world. Ion concentrations measured at 2 meter above ground
9 are typically in the range of 500 to 1000 cm^{-3} (Hirsikko et al., 2011). In summer 2013,
10 measurements with an air ion spectrometer (AIS) were performed at the same clearing at the
11 “Waldstein” site. The AIS is very similar to the NAIS, except that it is not equipped with a
12 corona charger for charging the neutral particles. Measurements with the AIS resulted in
13 typical positive and negative cluster ion concentrations of 600 and 900 cm^{-3} , respectively.
14 These values compare much better with the concentrations published by Hirsikko et al.
15 (2011), and range close to the upper end of typical values. The obvious discrepancy between
16 the AIS and NAIS may be explained by different inlets of the two instruments. The inlet of
17 the NAIS was 1.8 m long and was bent by 180°, while the AIS inlet was about 1 m long and
18 had a bending of only 90°. An enhanced ion loss in the NAIS inlet due to diffusion is
19 probable, as the penetration for cluster ions through the NAIS inlet is only about half of the
20 penetration through the AIS inlet. Further, electrostatic losses for the NAIS measurements
21 could give an explanation for the generally lower concentrations of negative ions in compare
22 to positive ions. Negative ions have a higher electrical mobility and are therefore
23 preferentially lost due to a present electro static field. Considering the much higher ion
24 concentrations and the optimized inlet of the AIS, absolute ion concentrations measured with
25 the NAIS in 2012 are probably underestimated. However, the underestimation of the absolute
26 concentration does not affect the determination of the growth rates with the maximum
27 concentration method.

28 The median ionization rates Q determined with the NAIS during NPF events are 0.8 and
29 0.9 $\text{cm}^{-3} \text{s}^{-1}$ for negative and positive cluster ions, respectively (cf, Tab. 2). The calculated Q s
30 are most probably underestimated since Q depends directly on ion concentrations, which are
31 underestimated by the NAIS. Furthermore, the simplified balance equation for determining Q
32 does not consider all active ion sinks, resulting in a general underestimation of about a factor

1 of 2 (Hörrak et al., 2008). Considering these facts, Q was probably well above 3 ion pairs
2 $\text{cm}^{-3} \text{s}^{-1}$ during summer 2012 at “Waldstein”.

3

4 **3.3 Time difference**

5 In all 8 evaluated NPF events, 2 nm ions (NAIS size bin limits were 1.8 – 2.1 nm) showed a
6 concentration increase before the concentrations of total particles of the same size increased.
7 Fig. 4 (a) shows the course of concentration for 2 nm total particles and ions for an exemplary
8 NPF event on 12 August, 2012. The occurrence of an earlier ion formation prior to total
9 particle formation seems to be a typical pattern during NPF. Manninen et al. (2010) report of
10 NAIS measurements during NPF at several locations in Europe. They also observed the
11 earlier formation of 2 nm ions prior to 2 nm total particle formation in different environments.
12 However, this behavior was not investigated in more detail in other studies. When considering
13 the concentrations of larger particles and ions, the time gap between the appearance of
14 charged and total particles becomes smaller with increasing particle size (Fig. 4 b-e). This
15 behavior was observed throughout all NPF events considered in our study. In order to
16 determine the time difference Δt between the appearance of ions and total particles, a cross-
17 correlation analysis was performed individually for each size class. Cross-correlation analysis
18 is a standard procedure to analyze time shifts in two time series. The result of the cross-
19 correlation analysis can be seen in Fig. 5. For small particles, Δt is largest and sharply
20 decreases as the particle diameter increases, eventually reaching $\Delta t = 0$ for diameters of about
21 20 nm. Therefore, the total particles seem to grow faster than ions after the onset of a NPF
22 event, as Δt becomes smaller during the growth process.

23

24 **3.4 Growth rates**

25 Due to the decrease of Δt during NPF, GR_t is expected to differ from GR_{neg} and GR_{pos} ,
26 especially when considering small particle diameters. In fact, our analysis yields an increased
27 GR_t compared to GR_{neg} and GR_{pos} . At this point, it should be mentioned once more that the
28 growth rates above an ion/particle diameter of 20 nm are most probably overestimated by the
29 maximum concentration method. Fig. 6 (a) shows the growth rates for the NPF event on 4
30 July, 2012. GR_{neg} and GR_{pos} are similar to each other, while the total particles grow faster.

1 Fig. 6 (b) shows the median growth rates of all 8 regional NPF events. An enhanced GR_t is
2 evident in the median values. The enhanced GR_t compared to charged particle growth rates
3 deviates from theories for pure condensational growth, where the presence of a charge
4 enhances the growth rates of small and intermediate ions (e.g. Yu and Turco, 2000; Yue and
5 Chan, 1979). Therefore, condensational growth on its own cannot explain the apparent GR
6 differences. To further support our observations at the “Waldstein” site, we analyzed
7 additional data recorded with a NAIS instrument during summer 2008 at the “Melpitz” field
8 site in NW Saxony, Germany. In these data, the same patterns are found: Δt decreases during
9 the growth process and total particles show an enhanced growth rate compared to ions. As the
10 determination of the growth rates is always connected to some error, the enhancement of GR_t
11 over to GR_{neg} and GR_{pos} cannot be regarded as significant, but still it is considered to be
12 plausible.

13

14 **3.5 Recombination**

15 The number size distributions deduced from ion-ion recombination as described by Eq. 1 are
16 generally comparable to the measured total particle distributions. However, the resulting
17 absolute concentrations of particles from ion-ion recombination are one to three orders of
18 magnitude smaller than the observed total particle distributions. Particularly, when diameters
19 below 10 nm are considered, recombination cannot explain the abundance of total particles
20 (cf. Fig. 2). This may be partly due to the performance of the NAIS. As described in section
21 3.2 ion concentrations in our study are generally underestimated, while an overestimation of
22 total particle concentrations is a typical property of NAIS instruments (Gagné et al., 2011).
23 Therefore, the absolute values are not taken into consideration for our study. Nevertheless, the
24 recombination gives valuable information regarding the growth behavior of neutral particles.
25 A measure which can still be used for our analysis is the growth rate of the recombination
26 products (GR_{rec}). As mentioned above, GR_t is elevated at small particle diameters compared
27 to GR_{neg} and GR_{pos} . GR_{rec} seems to behave similar to GR_t as can be seen in Figs. 2 and 6. For
28 most of the NPF events considered in our study, GR_{rec} is well above GR_{neg} and GR_{pos} (Fig.
29 6 b) and sometimes matches GR_t quite well (Fig. 6 a).

30

1 **4 Discussion**

2 The 8 particle formation events at the “Waldstein” site considered in this study can be
3 separated into two distinct stages. The formation of the first stable clusters and particles seem
4 to happen in the ion fraction. Later, the ion formation step is followed by a very intense
5 formation and growth of neutral clusters and particles. The initial ion induced nucleation (IIN)
6 typically happens about 20 - 30 minutes before the first appearance of neutral particles (Fig. 5
7 c, d; Tab. 2) at “Waldstein”. This observation can most likely be explained by the higher
8 stability of charged clusters over neutral ones at a certain precursor gas saturation ratio
9 (Enghoff and Svensmark, 2008; Yue and Chan, 1979). Furthermore, charged clusters clearly
10 activate more easily and grow more quickly (e.g. Lushnikov and Kulmala, 2004; Winkler et
11 al., 2008; Yu and Turco, 2000). Keeping this in mind and assuming no ion-ion and ion-
12 particle interactions, the time difference between an earlier occurring ion fraction and the total
13 particle fraction during the growth process should increase or remain constant. However, our
14 measurements show a contrary behavior: once formed, the neutral particles grow considerably
15 faster than the ion fraction, and eventually, the earlier occurrence of the ions vanishes
16 completely. A possible explanation for the slower ion GR could be the diurnal variation of gas
17 phase precursors like sulfuric acid or oxidation products of volatile organic compounds
18 (VOC). In the early morning hours, when the first intermediate ions are formed, the precursor
19 gas concentrations are expected to be low. On sunny days, as were most of the considered
20 event days, the precursor gas concentration will increase during the day. This is due to
21 increasing VOC emissions from the forest with rising air temperature, as well as due to
22 photochemical processes leading to the formation of sulfuric acid and oxidation of VOCs.
23 Therefore, the neutral particle growth which occurs later could be enhanced due to higher
24 concentrations of precursor gases.

25 Additionally, ion-ion and ion-particle interactions enhance neutral particle GRs. As the
26 potential precursor gases were not measured in this study, the focus to explain our observation
27 will be on ion-particle interaction processes. Nevertheless, it is not expected that the
28 observations can be explained fully by ion-particle interactions.

29 Considering ion-particle interactions by applying theoretical parameterizations of the
30 attachment and recombination processes to the combined NAIS and mobility particle size
31 spectrometer measurements, we obtained the ion-mediated or -recombined fraction of neutral
32 particles. NAIS number concentration measurements are subject to uncertainties both for ions

1 and total particles (Asmi et al., 2009; Gagné et al., 2011). However, growth rate analyses are
2 not influenced by the uncertainties in NAIS number concentrations. Therefore, we chose
3 GR_{rec} deduced from the calculated recombination number size distribution as a measure for
4 the influence of ions on neutral particle formation.

5 In general, our analyses show an earlier formation of charged particles compared to total
6 particles (Fig. 5). When looking more closely at the time difference of appearance (Δt) of ions
7 and total particles, the 8 considered NPF events can be divided in two classes: (1) initial Δt is
8 larger than 20 minutes (Fig. 7) and (2) initial Δt is smaller than 20 minutes (Fig. 8).

9 Median values of four NPF events (04 July; 23 July; 24 July; 12 August 2012; cf. Tab. 2) with
10 $\Delta t > 20$ minutes are shown in Fig. 7. The large differences in the growth rates for ions and
11 total particles (Fig. 7 a) are remarkable. While GR_{neg} and GR_{pos} are as expected for small
12 diameters, GR_t for small total particles is strongly elevated (cf. Tab. 2). This strong growth is
13 maintained until a sharp drop for diameters above 10 nm is evident. The unusual sharpness of
14 the decrease can most likely be attributed to limitations of the maximum concentration
15 method and the inversion routine of the NAIS. Nevertheless, qualitatively the decrease in GR_t
16 is considered real, indicating a change in the prevailing growth conditions. Fig. 7 (b) shows
17 the time evolution of the growing mode's diameter of maximum concentration (Dp_{max}) for
18 both ion polarities as well as for total particles. More specifically, Dp_{max} is the result of the
19 maximum concentration method for the determination of the growth rates (cf. black lines in
20 Fig. 2). The origin of the horizontal axis (time = 0) indicates the first appearance of the total
21 particle growing mode. The time of initial ion appearance is offset by the median of Δt at 2
22 nm for positive and negative ions, respectively (cf. Fig. 7 c, d). The initial offset of the ion
23 growing mode is about 60 minutes. As total particles exhibit a higher GR_t , their growing
24 mode finally reaches the same Dp_{max} as the ion modes, about 40 to 60 minutes after the first
25 appearance of total particles.

26 Fig. 7 (c) and (d) show the time difference (Δt) in occurrence of ions compared to total
27 particles. Δt exhibits a rapid decrease as the particles grow. Eventually, for particle diameters
28 above 10 nm, the advance of ions is fairly small and continues to decrease at a slower rate, to
29 approach $\Delta t = 0$ at about 20 nm. Additionally, Fig. 7 (c) and (d) show the independently
30 derived time difference between the negative and positive Dp_{max} to the total one (cf. Fig. 7 c,
31 d as black dotted lines). Basically, this is a comparison of Δt derived from the cross-
32 correlation method with the time difference derived from the maximum concentration

1 method. The general patterns of these time differences are very similar: the rapid decrease of
2 Δt is clearly evident until particle diameters of about 10 nm are reached. For greater particle
3 diameters the time differences of $D_{p_{\max}}$ become negative, indicating a persistently enhanced
4 growth rate of the total particle growing mode. However, our data do not show an advance of
5 the total growing mode compared to the ion modes (cf. Figs. 4, 5 and 7 c,d). This discrepancy
6 may be explained by the increasing uncertainty associated with the growth rate determination
7 for larger diameters.

8 Median values for four NPF events with $\Delta t < 20$ minutes (17 June; 19 June; 13 August; 17
9 August 2012; cf. Tab. 2) are shown in Fig. 8. The median growth rates for these events (Fig. 8
10 a) are significantly lower compared to the high growth rates presented in Fig. 7. Additionally,
11 there is no visible difference in GR_{neg} , GR_{pos} and GR_t . They exhibit similar values throughout
12 the whole growth process (cf. Tab. 2). Typically, 2 nm positive and negative ions show an
13 earlier appearance (Δt) of about 15 and 10 minutes, respectively (Fig. 8 c, d). The decrease of
14 Δt during the growth process is relatively slow. Nevertheless, the diameter at which Δt
15 approaches zero is still at about 20 nm. The time needed for the total particle mode to grow to
16 this size is approximately 200 minutes (Fig. 8 b). The time difference deduced from $D_{p_{\max}}$
17 becomes negative at a diameter of about 20 nm, supporting the assumption that growth rates
18 above this diameter are overestimated. As Δt shows a slow decrease during the growth
19 process, GR_t should be slightly enhanced compared to GR_{neg} and GR_{pos} . This is not visible in
20 our data. Presumably, the accuracy of the applied growth rate determination is not sufficient
21 to resolve such slight differences.

22 As the absolute contribution of ion-ion recombination and ion-particle attachment to NPF is
23 not quantitatively assessed in this work we propose a conceptual mechanism governing our
24 observations. Fig. 9 shows the conceptual model for interactions of positive cluster ions (red)
25 with the negative growing ion mode (blue), the neutral background particles and the neutral
26 growing mode (both black). For illustrational purposes, we will focus on the ion attachment
27 (green dashed lines) and the recombination of cluster ions with the growing ion mode (yellow
28 dashed lines) and neglect the recombination of cluster ions with each other.

29 At the onset of NPF (Fig. 9 a), first particles are formed in the ion fraction, exhibiting
30 concentrations in the order of 10^1 cm^{-3} . Ion-ion recombination occurs among cluster ions and
31 the freshly nucleated ion mode (yellow dashed line). Additionally, the background aerosol
32 particles, exhibiting concentrations in the order of 10^3 cm^{-3} , are available for the attachment of

1 cluster ions (green dashed line). Considering the recombination coefficient α at 2 nm and the
2 attachment coefficient β at 100 nm (cf. Fig. 1, yellow and green solid lines), the probabilities
3 for cluster ions to interact with the growing ion mode and with the neutral background
4 particles are approximately the same. As the background aerosol is more numerous than the
5 freshly nucleated ion mode, attachment to the background particles dominates over
6 recombination. Hence, only a very small number of neutral particles are formed by
7 recombination.

8 Once precursor gas phase components are available in a sufficient quantity for neutral
9 nucleation (cf. Almeida et al. 2013; Kulmala et al., 2013; Schobesberger et al., 2013), a strong
10 nucleation burst of neutral particles occurs (Fig. 9 b). The freshly nucleated neutral mode has
11 a very small mean diameter (e.g. 1.5-2 nm) and shows typical concentrations in the order of
12 10^3 cm^{-3} . The background particle number size distribution stays mostly unchanged ($D_p > 100$
13 nm; 10^3 cm^{-3}). Now, the neutral nucleation mode and the background particles are available
14 for the attachment of cluster ions. Meanwhile, the ion mode has grown to a greater diameter
15 (e.g. 4 nm), exhibiting only a slightly enhanced number concentration still in the order of
16 10^1 cm^{-3} . β for cluster ion attachment to the background particles is elevated by 2 orders of
17 magnitude compared to the neutral nucleation mode (cf. Fig. 1). Therefore, cluster ion
18 attachment to the background particles dominates over the attachment to the neutral
19 nucleation mode, as both modes have similar concentrations. On the other hand, α for cluster
20 ions with the growing ion mode is elevated by 2 orders of magnitude compared to β for the
21 neutral growing mode. As the neutral mode exhibits approximately 2 orders of magnitude
22 more particles, the absolute number of cluster ions recombining with the ion mode is
23 comparable to the number of ions attaching to the neutral mode. In other words, background
24 particles are charged strongly (bold red arrow), the neutral nucleation mode experiences
25 moderate charging (red arrow) and the formation of neutral particles by recombination is also
26 moderate (black arrow). This moderate formation of somewhat greater neutral particles from
27 recombination contributes to the growth of the neutral mode. On the other hand, the ions
28 formed by attachment to the neutral mode are somewhat smaller than the mean ion mode
29 diameter, and contribute to a slower growth of the ion mode. The absolute production of
30 neutral and charged particles by this mechanism depends on the concentration of cluster ions
31 as well as on the concentration of the growing ion- and neutral modes, and is thought to be in
32 the order of $0.01 \text{ cm}^{-3} \text{ s}^{-1}$.

1 As the growth continues, the neutral particle mode reaches a number concentration peak
2 (order of 10^4 cm^{-3}) at diameters of approximately 4 - 5 nm (Fig. 9 c). Due to the high
3 concentration, the attachment probability of cluster ions to the neutral nucleation mode and
4 the background particles is similar (green dashed lines). Meanwhile, the ion mode has grown
5 further (e.g. 6 nm diameter), and is slightly more numerous but still in the order of 10^1 cm^{-3} .
6 Therefore, recombination is somewhat enhanced compared to stage (b). Nevertheless, the
7 neutral nucleation mode experiences a stronger loss of particles due to attachment of cluster
8 ions. As a result, the concentration of the growing ion mode is further enhanced by the
9 addition of somewhat smaller charged particles. Again, the loss of ions (due to
10 recombination) and the addition of newly formed smaller ions (due to attachment) results in
11 an apparent growth rate reduction of the ion mode. On the other hand, the concentration of the
12 neutral mode is constantly reduced, while its growth rate stays elevated.

13 Finally, the diameters of the neutral and ion growing modes approach each other (Fig. 9 d).
14 By this time the concentration of the ion mode is further enhanced (10^2 cm^{-3}) and the neutral
15 mode concentration has decreased to about 10^3 cm^{-3} . The converging concentrations and
16 similar diameters result in a comparable magnitude of attachment and recombination to the
17 ion and neutral growing modes. As the neutral particles (formed from recombination) and the
18 charged particles (formed from attachment) have approximately the same diameter, an
19 enhancement or slowing of the growth rates is not expected. This results in an equilibrium
20 state where ions and neutral particles grow at similar rates.

21

22 **5 Conclusions**

23 Data from 8 NPF events measured with the NAIS at the “Waldstein” site showed an earlier
24 appearance of the ion modes in the beginning of NPF and a higher initial growth rate of the
25 “delayed” total particle mode in comparison to the ion modes. The enhanced growth of the
26 total particle mode does eventually result in the disappearance of the ion’s advance. To our
27 knowledge, such differences of ion and total growth rates in the initial stages of cluster
28 growth have not been presented before. Therefore, it is an interesting yet open question if
29 these observations are just a special feature of the “Waldstein” site, or if they can also be
30 found elsewhere. An earlier appearance of the ion mode is plausible, as ions reduce the
31 critical cluster size and facilitate the cluster activation (e.g. Lushnikov and Kulmala, 2004;
32 Winkler et al., 2008; Yu and Turco, 2000; Yue and Chan, 1979). To, at least partly, explain

1 the difference in the growth rates we have proposed a mechanism including ion-ion
2 recombination and ion-particle attachment (cf. Fig. 9).

3 Due to limitations of our measurement equipment (detection limit for neutral particles ~
4 2 nm), no direct conclusions on the influence of ions on neutral particle nucleation can be
5 deduced at the size range where the onset of NPF occurs. As stated by Kontkanen et al.
6 (2013) and Kulmala et al. (2013), pure cluster ion recombination is not thought to be of
7 sufficient magnitude to explain the intense neutral nucleation bursts. Further, Manninen et al.
8 (2010) reported that ion induced nucleation does only contribute about 10 - 13 % to NPF.
9 Nevertheless, ion interactions may play an important role in NPF by simultaneously
10 enhancing the neutral particle growth rate and reducing the ion growth rate. However, the
11 proposed mechanism is only valid in environments where the ionization rate (Q) is strong
12 enough to provide sufficient cluster ions for recombination and attachment.

13

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1 Appendix

2

3 According to Tammet and Kulmala (2005), the size dependent coagulation coefficient K_{ij} is
4 defined as

5

$$6 \quad K_{ij} = \frac{2\pi kT(B_i+B_j)(D_i+D_j+2h)}{1+\gamma-\frac{0.299\gamma}{\gamma^{1.1+0.64}}+\gamma\frac{1-p}{p}}, \quad (A1)$$

7 where

$$8 \quad \gamma = 2 \frac{B_i+B_j}{D_i+D_j+2h} \sqrt{\frac{2\pi kTm_i m_j}{m_i+m_j}}. \quad (A2)$$

9

10 Here, k is the Boltzmann constant [$1.38 \times 10^{-23} \text{ J K}^{-1}$], T is the absolute temperature [K], B is
11 the particle's mechanic mobility [$\text{m N}^{-1} \text{ s}^{-1}$] (Hinds, 1999), D is the particle diameter [m], the
12 sticking probability p was assumed to be one, and m is the mass of an individual particle [kg].
13 To account for van der Waals interactions, an extra distance $h = 0.115 \times 10^{-9} \text{ m}$ is necessary
14 (Tammet and Kulmala, 2005). The variability of the size-dependent coagulation coefficient
15 due to a 20 % change in B , a doubling reduction to 50 % of h and the variation of p between
16 0.5 and 1 is depicted as shaded areas in Fig. 1. The sticking probability exhibits the most
17 pronounced influence on the values of K_{ij} , while the other two variables only show a minor
18 effect.

19

20 An approximation for the size dependent attachment coefficient β_{ij} is given by Hörrak et al.
21 (2008):

22

$$23 \quad \beta_{ij} = \frac{2\pi D_i kT Z_j}{e} \frac{x}{\exp(x)-1} \sqrt{1 - \frac{2}{2+n(n-1)+D_i/(10 \text{ nm})}}, \quad (A3)$$

24 where,

$$25 \quad x = \frac{ne^2}{2\pi D_i \epsilon_0 kT}. \quad (A4)$$

26

1 Here, Z is the electric mobility of the ion provided by the NAIS [$\text{m}^2 \text{V}^{-1} \text{s}^{-1}$], e is the
 2 elementary electric charge [$1.6 \times 10^{-19} \text{C}$], n is the number of elementary charges carried by a
 3 charged particle, and ϵ_0 is the electric constant [$8.85 \times 10^{-12} \text{F m}^{-1}$]. The variability of β_{ij} was
 4 assessed by varying Z in the range of the bin width of the respective NAIS size channel (cf.
 5 Fig. 1).

6

7 For the interaction of oppositely charged ions of size j and k , a size dependent recombination
 8 coefficient α can be described by the attachment coefficient β_{jk} (Hoppel and Frick, 1986).

9 Therefore, the recombination coefficient (α_{jk}) is defined equally to the attachment coefficient,
 10 but only for oppositely charged ions:

11

$$12 \quad \alpha_{jk} = \beta_{jk}. \quad (\text{A5})$$

13

14 The coagulation sink is calculated according to Kulmala et al. (2012):

15

$$16 \quad \text{Coag}S_i = \sum_{l=i}^{l=\text{max}} K_{il} N_l, \quad (\text{A6})$$

17

18 where N_l is the number concentration of the background aerosol [cm^{-3}] in the size class l .

19

20 The calculation of the charging sink follows Eq. 3 from Hörrak et al. (2008):

21

$$22 \quad \text{Char}S_i^\pm = p_i \sum_j \beta_{ij} N_j^\pm, \quad (\text{A7})$$

23

24 where, p_i is the probability of a neutral particle in size class i to carry one elementary charge
 25 and N_j^\pm is the number concentration of positive or negative ions in size class j [cm^{-3}].

26

27 Hoppel and Frick (1986) proposed a simplified balance equation for the cluster ion production
 28 rate. For our work, we use a slightly altered version, not assuming symmetric concentrations
 29 of positive and negative small ions and considering size-dependent attachment and
 30 recombination coefficients. The balance equation for the ionization rate Q^\pm is defined as:

31

$$1 \quad \frac{dN_{<1.6 \text{ nm}}^{\pm}}{dt} = Q^{\pm} - \sum_{jk} \alpha_{jk} N_j^{+} N_k^{-} - \sum_{ij} \beta_{ij} p_i N_i N_j^{\pm}, \quad (\text{A8})$$

2

3 where size classes j and $k < 1.6 \text{ nm}$, N_j^{+} and N_k^{-} are positive and negative ion concentrations

4 in size class j and k [cm^{-3}], N_i is the concentration of neutral particles in size class i [cm^{-3}] and

5 $N_{<1.6 \text{ nm}}^{\pm}$ is the number concentration of positive or negative ions with a diameter below

6 1.6 nm [cm^{-3}].

7

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1 Tab. 1: Median, 25th and 75th percentile of cluster ion concentrations [cm⁻³] (diameter <
 2 1.6 nm) during 8 selected NPF event and 13 non-event days, measured with the NAIS during
 3 summer 2012 at the “Waldstein” site.

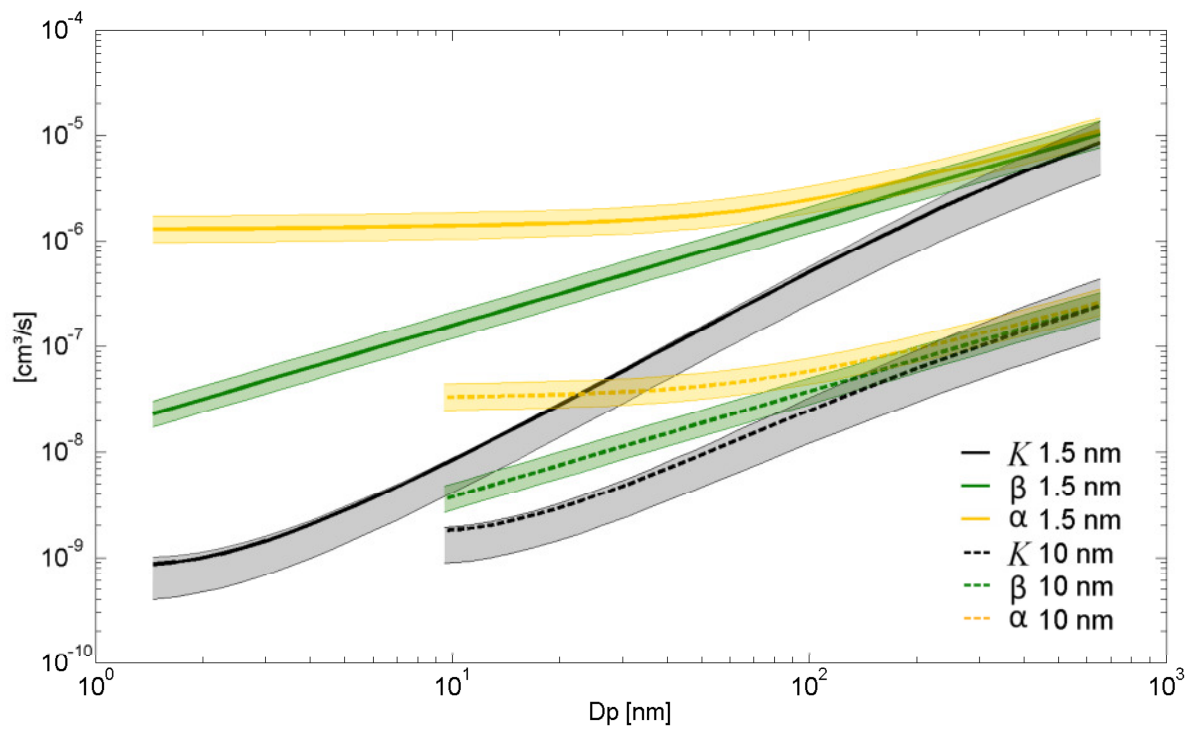
	Median	25 th	75 th
Non-event negative	129	101	186
NPF-event negative	148	126	176
Non-event positive	314	252	422
NPF-event positive	339	285	395

4

1 Tab. 2: Event features of all 8 selected NPF events used for this study. Shown are: NPF event
2 start time (CET), prevailing wind direction, time difference Δt of 2-3 nm ions [min.], growth
3 rates GR of 2-3 nm total particles and ions [nm h^{-1}], formation rates J of 2-3 nm total particles
4 and ions [$\text{cm}^{-3} \text{s}^{-1}$] and ionization rates Q for cluster ions [$\text{cm}^{-3} \text{s}^{-1}$]. Values for Q_{neg} , Q_{pos} , J_{neg}
5 and J_{pos} are probably underestimated, please refer to section 3.2 for detail.

Date	Start	Wind sector	Δt_{neg}	Δt_{pos}	GR _t	GR _{neg}	GR _{pos}	J_t	J_{neg}	J_{pos}	Q_{neg}	Q_{pos}
17 June 2012	13:00	W	20	5	2.8	6.3	3.2	0.4	0.02	0.02	0.4	0.4
19 June 2012	12:00	E	-62	0	1.5	2	1.9	0.4	0.002	0.006	0.5	0.7
04 July 2012	09:30	E	33	22	2.9	2.4	2.3	0.5	0.006	0.007	0.7	0.9
23 July 2012	07:30	E	102	97	5.3	1.5	1.4	5	0.02	0.02	0.9	1
24 July 2012	08:30	E	67	42	9	2.4	3.7	2.3	0.004	0.01	0.8	0.9
12 August 2012	08:30	E	53	38	6.9	3.2	3.8	4.7	0.02	0.04	1.1	1.2
13 August 2012	07:30	E	17	13	6	3.5	4.4	5.2	0.02	0.05	1.3	1.6
17 August 2012	08:30	E	10	5	1.6	1.6	1.8	5.2	0.01	0.02	0.8	0.8
Median	-	-	26.5	17.5	4.1	2.4	2.75	3.5	0.015	0.02	0.8	0.9

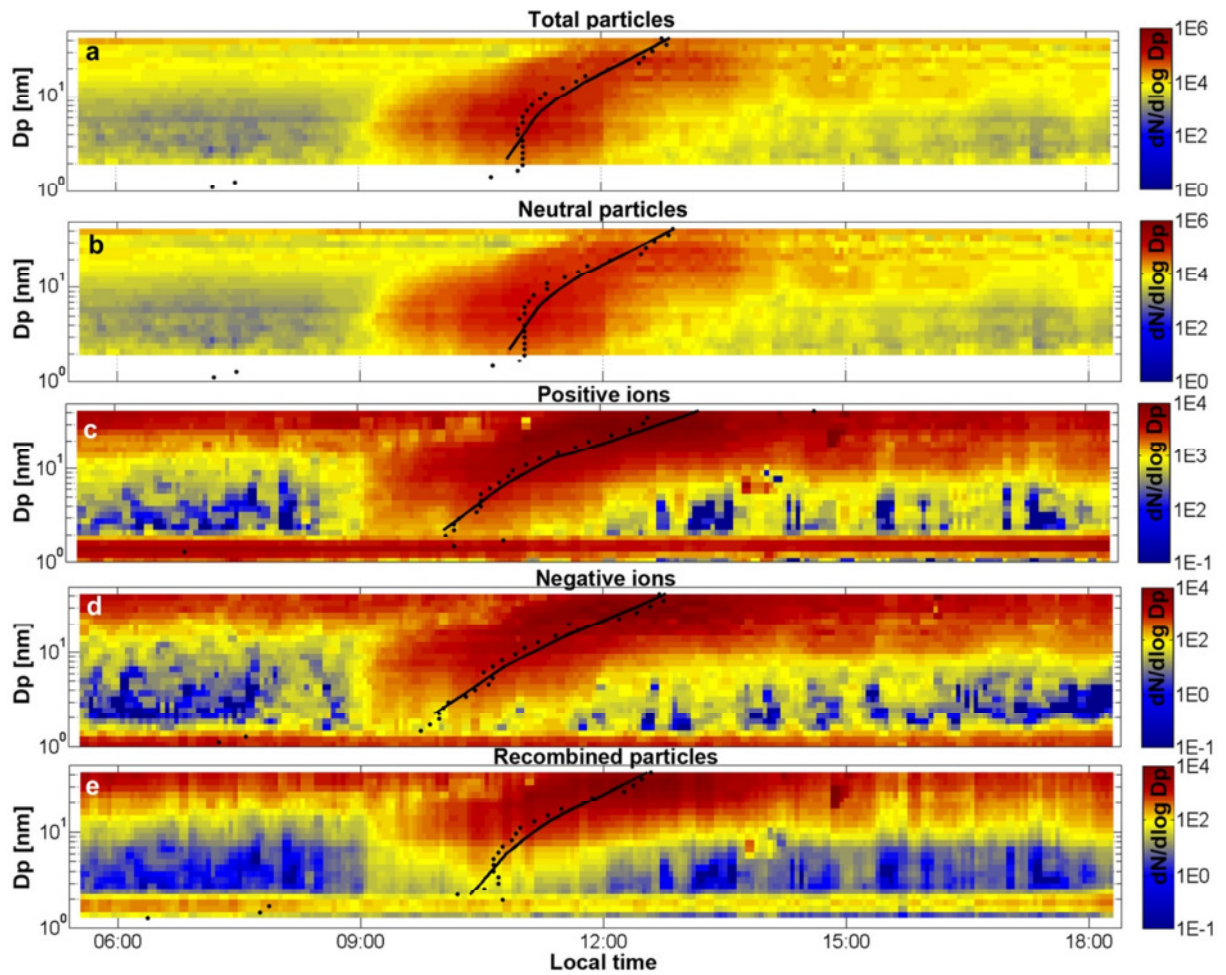
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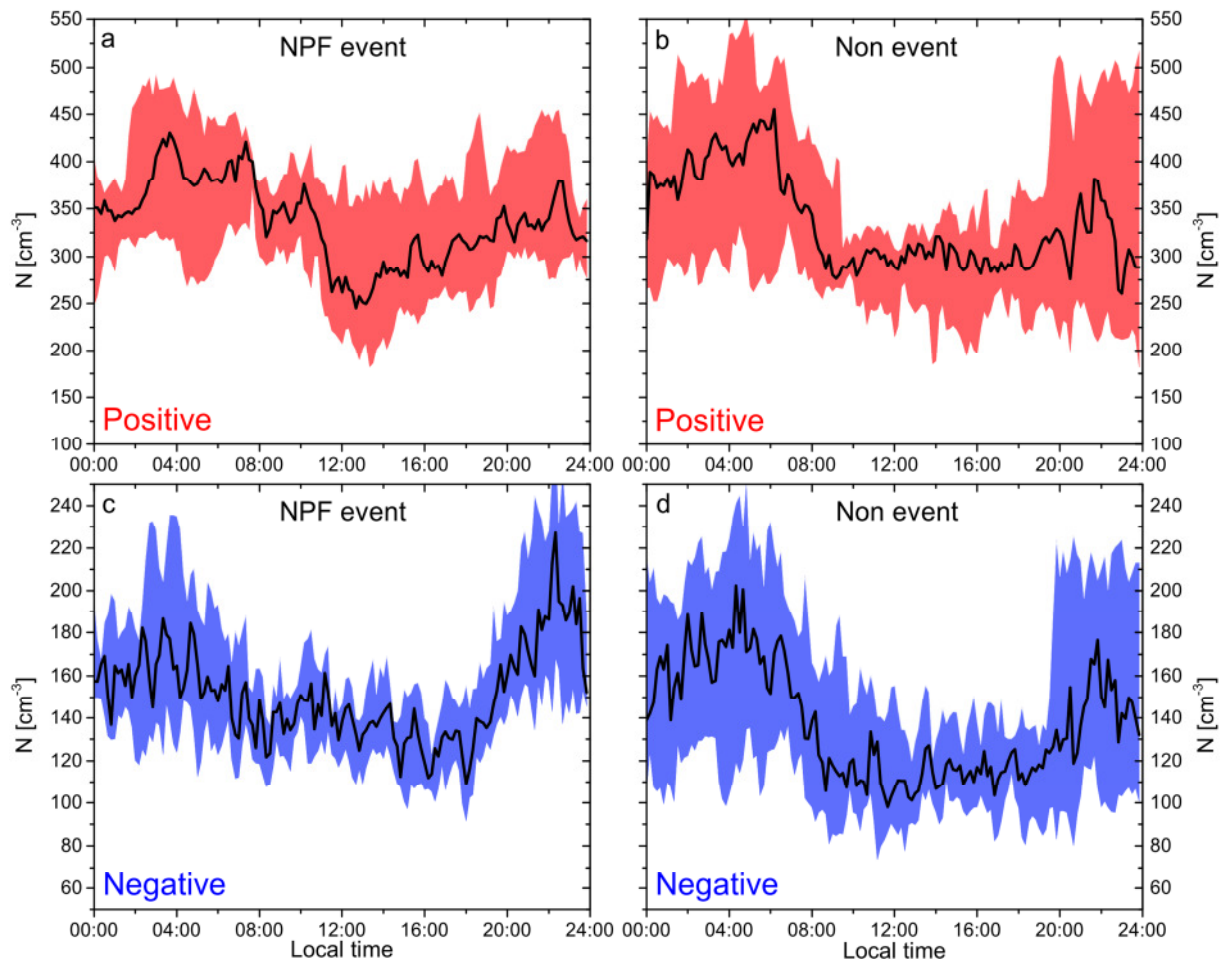
2 Fig. 1: Coagulation coefficient K , attachment coefficient β and recombination coefficient α
 3 [$\text{cm}^3 \text{s}^{-1}$] for small cluster ions and particles (1.5 nm, solid lines) and large ions and particles
 4 (10 nm, dashed lines) as a function of ion/particle diameter D_p . Shaded areas denote the
 5 variability of the respective coefficients, please refer to the appendix for details.

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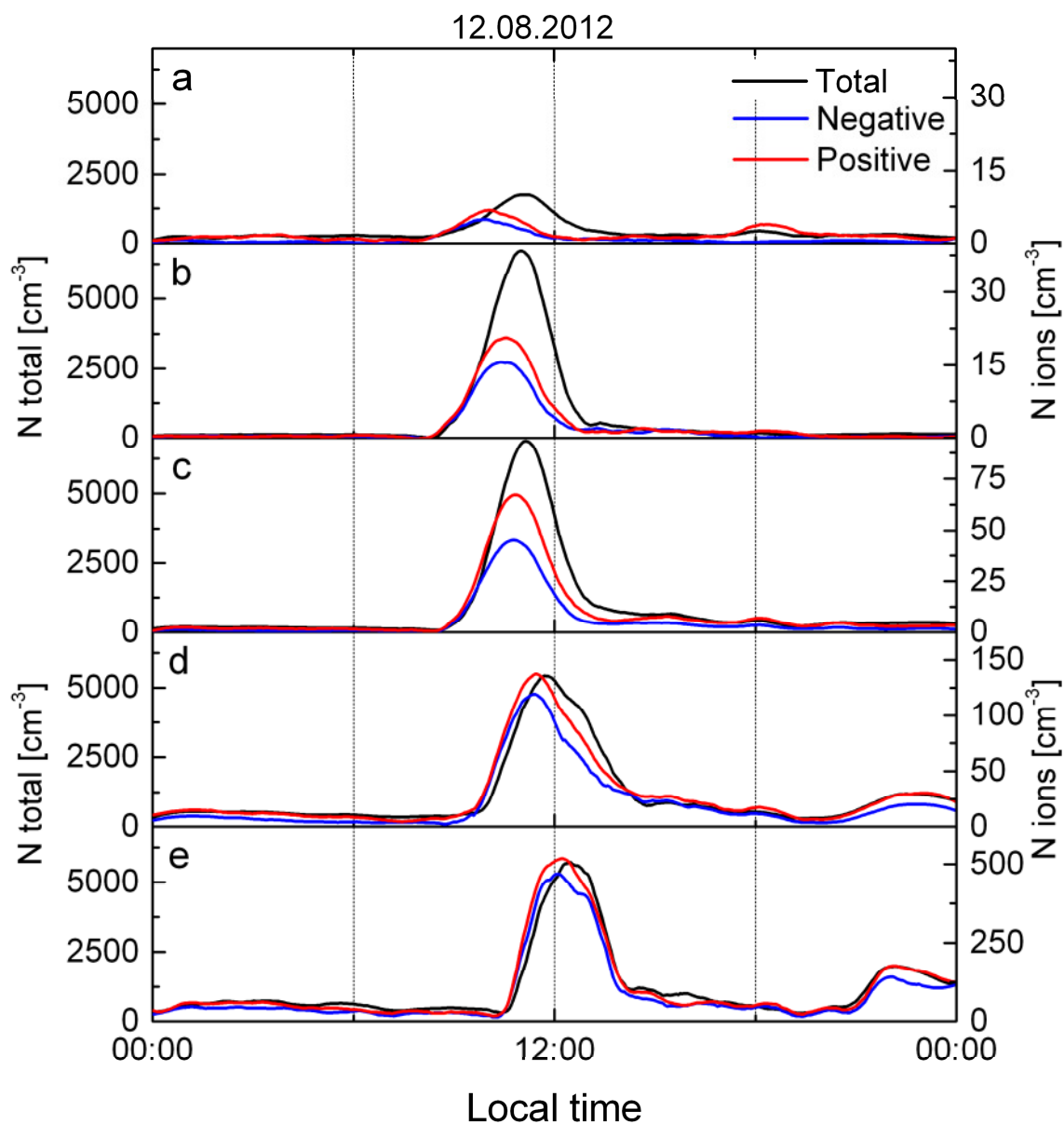
Fig. 2: NPF event of 12 August 2012 as measured with the NAIS. Shown are a) total particles, b) neutral particles, c) positive ions, d) negative ions and e) calculated neutral particles from ion-ion recombination. Black filled circles denote the concentration maxima for each size class, while black lines are smoothed fits in order to obtain continuous growth rates.



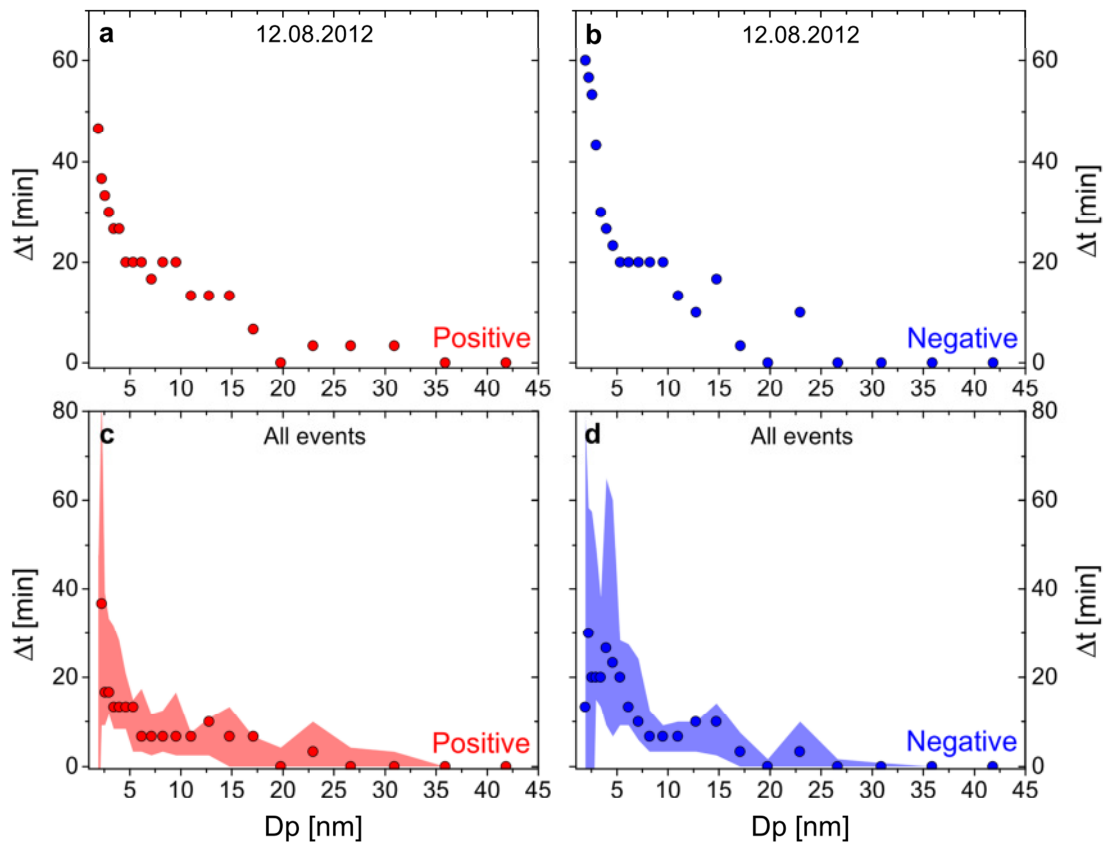
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2 Fig. 3: Median diurnal variation of cluster ion concentrations (diameter < 1.6 nm) during 8
 3 selected NPF event days (a, c) and 13 non-event days (b, d), as measured with the NAIS
 4 during summer 2012 at the “Waldstein” site. The shaded areas denote the 25th and 75th
 5 percentile.

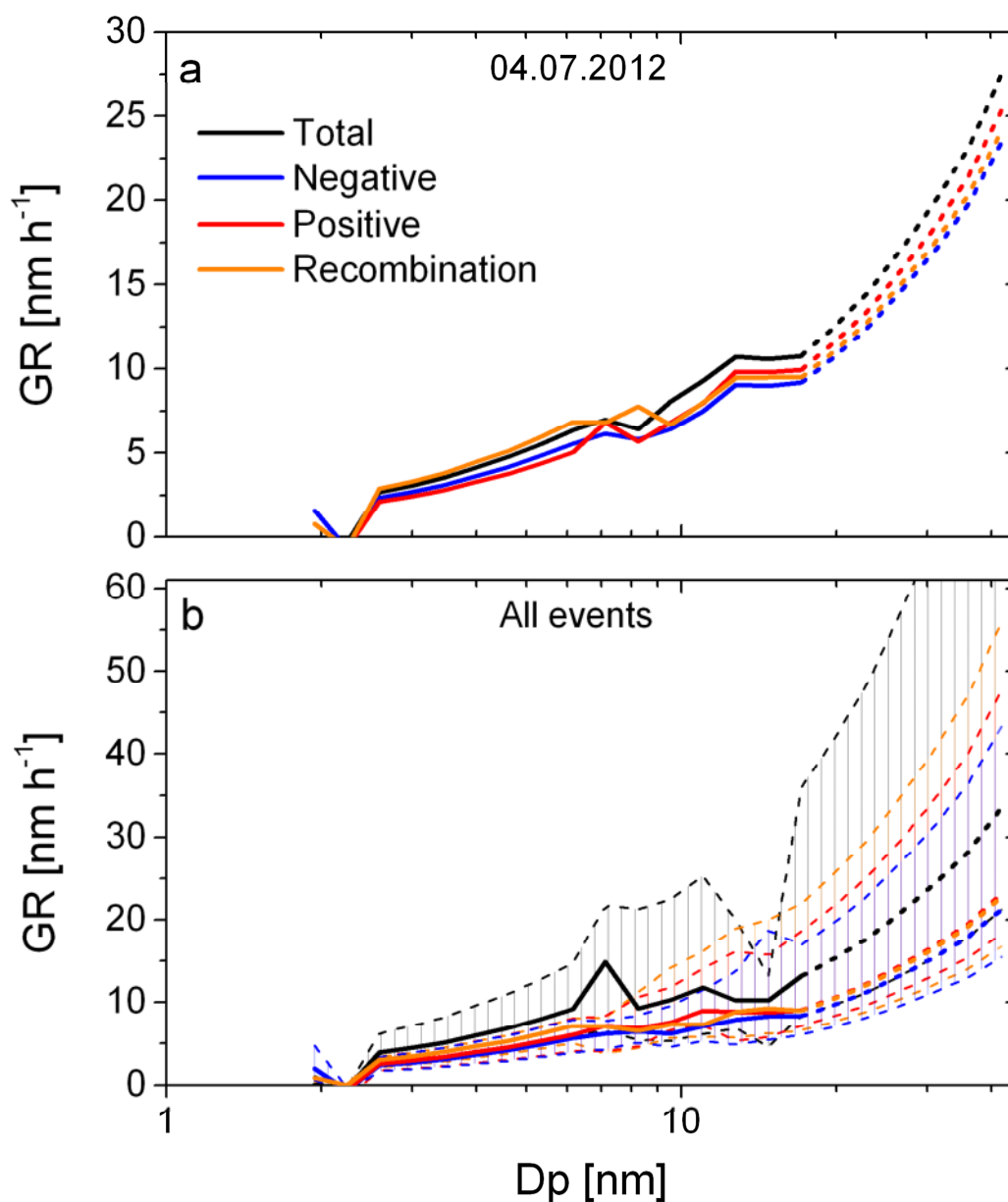
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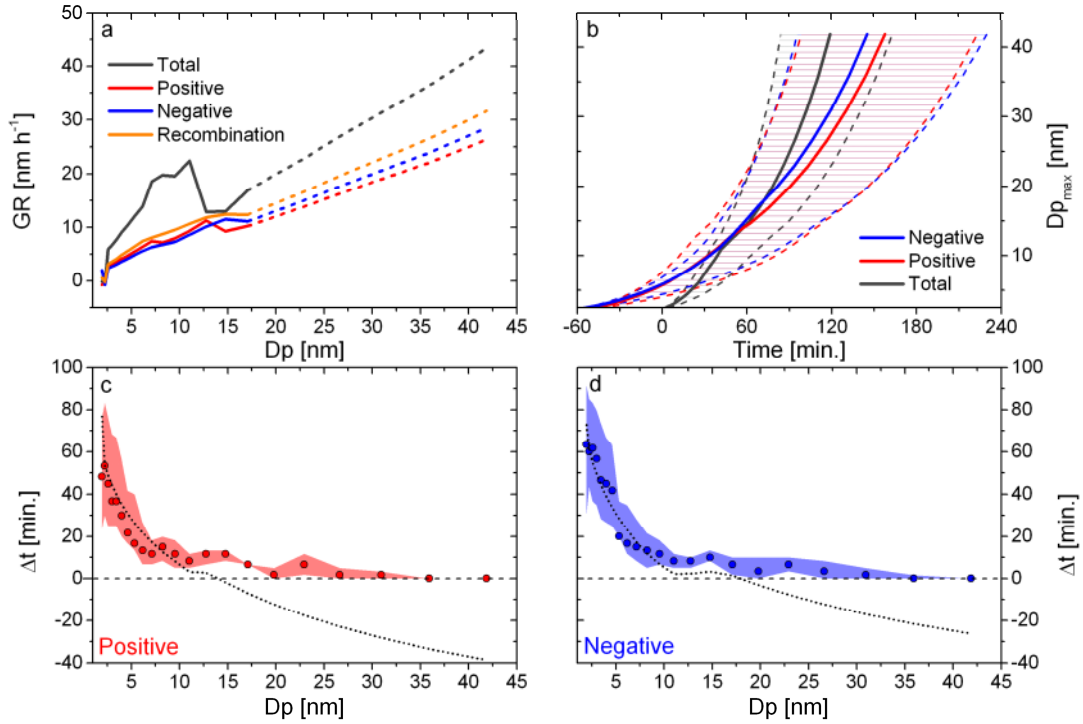
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 2 Fig. 4: Temporal evolution of total particle concentrations as well as positive and negative ion
 3 concentrations in diameter ranges of a) 1.8-2.1 nm, b) 3.7-4.3 nm, c) 7.6-8.8 nm, d) 13.6-15.7
 4 nm and e) 21.1-24.5 nm. The data originates from single NAIS size channels, measured
 5 during the NPF event on 12 August 2012 at “Waldstein”. Ion concentrations increase during
 6 the growth process, while total particle concentrations increase rapidly at the beginning of
 7 NPF but begin to decrease at diameters above 8 nm. Note that the ion concentrations (right
 8 axes) are always smaller than the particle concentrations (left axes). Data was smoothed for
 9 illustrational purpose.



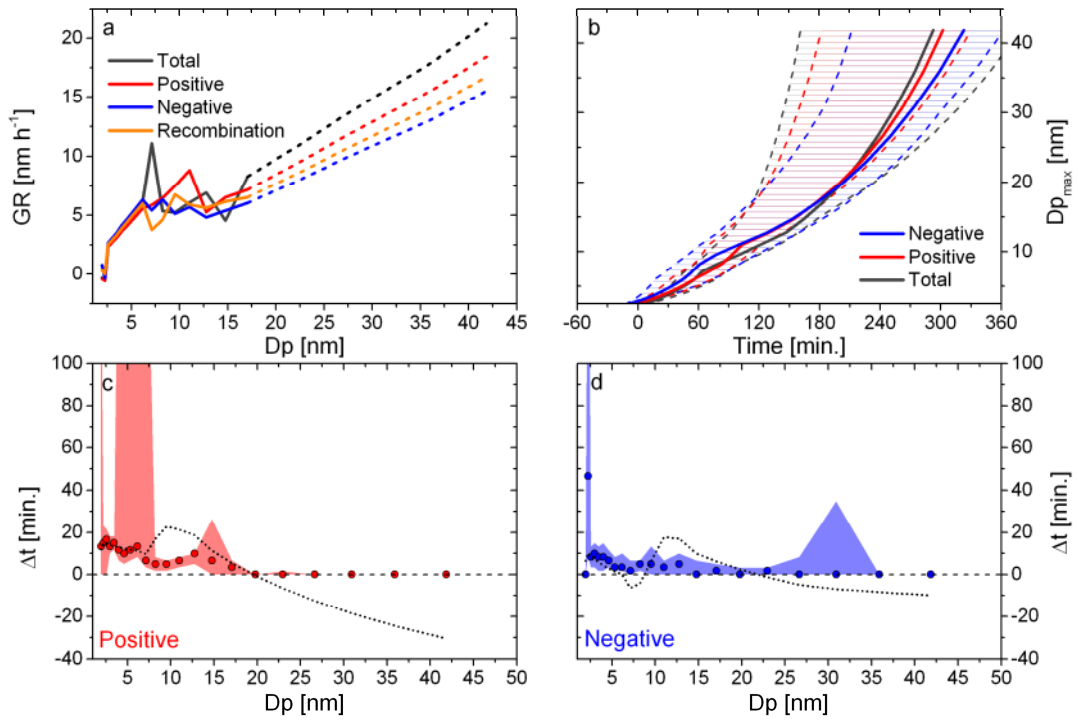
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 2 Fig. 5: Results from the cross-correlation study showing the size-dependence of the time
 3 difference (Δt). Appearance of a) positive and b) negative ions compared to total particles
 4 measured with NAIS on 12 August, 2012, and median values of Δt for all 8 selected NPF
 5 event days for c) positive and d) negative ions. Shaded area denote the 25th and 75th percentile
 6



1
 2 Fig. 6: Growth rates of negative ions, positive ions and total particles determined from NAIS
 3 measurements, a) for a single event on 04 July, 2012 and b) median values for all 8 selected
 4 NPF events used for this study. Hatched areas denote the 25th and 75th percentile.
 5 Additionally, GR_{rec} deduced from ion-ion recombination is shown in orange. Dashed
 6 segments of the curves denote inaccurate growth rates.
 7



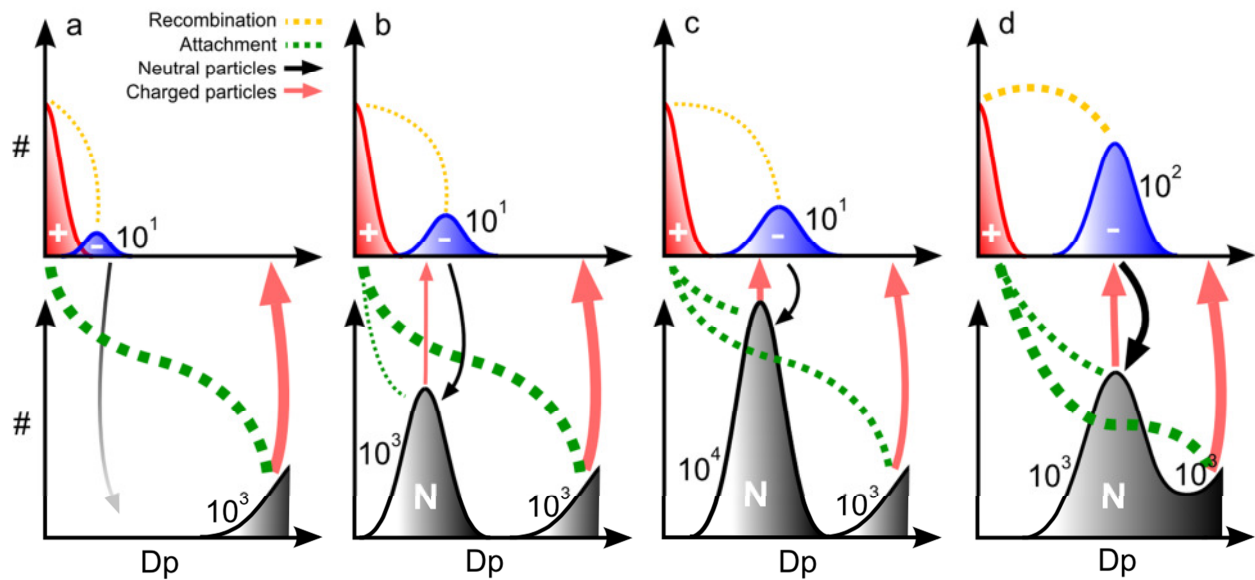
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 2 Fig. 7: Median evolution of ions and particles for four NPF events with $\Delta t > 20$ minutes. a)
 3 GR for total, positive, negative and recombined particles. b) Time evolution of the growing
 4 modes (Dp_{max}) of negative, positive and total particles, respectively. Hatched areas denote the
 5 25th and 75th percentiles. c, d) Time difference (Δt) for negative and positive ions,
 6 respectively. Dotted black lines are time differences calculated from the negative and positive
 7 growing mode to the total one, in principle this is the difference between the three Dp_{max} -
 8 values from section b).
 9



1

2 Fig. 8: Same as Fig. 7 but for four NPF events with $\Delta t < 20$ minutes.

3



1
 2 Fig. 9: Conceptual model of the influence of cluster ion recombination and attachment at
 3 different stages of particle nucleation and growth (a-d). Permanently available positive cluster
 4 ions are denoted in red, the negative growing mode in blue and neutral particle modes in
 5 black. The black and red arrows denote the generation of neutral and charged particles,
 6 respectively. The size of the arrows and dashed lines denotes the prevailing mechanism.
 7 Numerals indicate the orders of magnitude of the number concentrations of the respective
 8 modes.