Using measurements of the aerosol charging state in determination of the particle growth rate and the proportion of ion-induced nucleation

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We would like to thank the referees for the constructive comments to our manuscript. Below are our answers to the comments, separately for the three referees. Major additions to the text are also given here and marked using indentation. A few other noteworthy changes we have made to the manuscript are listed in the end.

Anonymous Referee #1
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This is a unique and important work. The authors came up with a novel way to evaluate the accuracy of the diameter growth rate (GR) obtained from the charged fractions, ion mobility distributions, and particle size distributions. The study on this topic requires reference GRs which are known to be accurate. The most of the reference GRs used in the previous studies were the modal GR obtained by analyzing the growth of particle size distribution (PSD) during the period of new particle formation (NPF). However, the modal GR may have significant measurement uncertainties and the modal GR might have significant bias from the true GRs; therefore, it has been difficult to validate the "the charged-fraction-approach" since accurate reference GRs have not been available. On the other hand, the authors of this paper generated accurate particle size distributions of electrically charged and neutral particles by numerical simulations of NPF events. The unknown in the numerical simulation is the growth rate of neutral and charged particles; therefore, the authors have applied previously suggested GR mechanisms in their numerical simulations and accounted for the potential variations in the charged fraction under different growth mechanisms, which is very clever. I strongly encourage that authors take advantage of this unique approach to continue evaluate the uncertainty and the bias of the GRs obtained from "the charged-fraction approach" under different types of NPF events observed over the globe.

I have only one general comment.

I suggest calculating the IIN+/- using the charged fraction obtained from the simulated results and GRs obtained by either fitting or iterated approach. Then, compare these IIN+/-with known IIN+/- from simulation.

In Sect. 4.1 of the manuscript we demonstrated that the initial charged fraction is not equal to the proportion of IIN because of the different removal rates of the neutral and charged particles with the different growth rates of the neutral and charged particles being most important process in this regard. Consequently, it makes sense to estimate the proportion of IIN from the determined initial charged fraction by taking the removal processes, especially the growth, into account. However, how this should be done is beyond the scope of this paper. Furthermore, the iteration and fitting methods are able to provide a growth rate that is assumed to be equal for neutral and charged particles, but separate growth rates for the neutral and charged particles is needed to estimate the proportion of IIN from the charged fraction.

On the other hand, the initial charged fraction and the proportion of IIN have been assumed to be equal in the previous studies. In order to provide some information on the accuracy of those studies, we have added an appendix (Appendix A; the old Appendix A is now Appendix B) in which we compare the initial charged fraction determined with the iteration method to the value of the proportion of IIN used as input in the model. Related to this addition, the first paragraph of Sect. 4.1 now reads:

> **The simulated fraction of charged particles at 1.8 nm was not the same as the fraction of particles formed carrying a charge ($IIN^{\pm}$). The formation of the particles was a source term of the particles at 1.8 nm, but the charged fraction depends on the concentrations of the neutral and charged particles, for which the sink terms had to be taken into account. Since the fitting and iteration methods provided estimates on the initial charged fraction, the values obtained using those methods were compared with the values of the charged fraction at 1.8 nm in diameter obtained directly from the simulations. However, since the initial charged fraction and the proportion of IIN have been assumed to be equal in previous studies (Laakso et al., 2007a; Gagné et al., 2008, 2010, 2012), we also compared the initial charged fractions determined with the methods to the proportions of IIN used as input in the model (Appendix A).**

Anonymous Referee #2
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General comments:
This study presents a comprehensive, detailed inter-comparison of published methods for obtaining aerosol dynamic properties (growth rate, charge fraction, relative contribution of ion-

induced nucleation) from measured size distributions of total and charged aerosol. The accuracy of those methods was determined by comparison with the output of an aerosol microphysical model under diverse, representative simulation conditions, yielding ranges of applicability for each method. The results of this study provide reasonable guidance for the application of these methods when studying ambient measurements. I recommend publication of this manuscript with minor corrections listed below.

Specific comments:
1. p. 21869, l. 15: The "certain conditions" that are mentioned here almost exclusively refer to laboratory experiments in which charged particles/ions are detected with a higher efficiency than their neutral counterparts. For the sake of clarity, consider stating explicitly that this charge preference for particle activation has been observed in laboratory experiments.

This part now reads:

> **In laboratory conditions, the ions have been observed to be activated more easily than similarly-sized neutral molecules or clusters and, furthermore, a sign preference in activation of the ions has been observed (Winkler et al., 2008).**

2. p. 21881, l. 17 – 20: It is not clear how the diameter dependence of the growth rate is accounted for since any size-dependence to the growth rate is lost when averaging over the size intervals in DR1 and DR2.

The fitting and iteration methods provide a single value of the growth rate for each simulation, so, in order to easily compare these values to those in the simulations, we need to determine a single value of GR also for the simulations. In most of the simulations the growth rate is diameter dependent, in which case we need to average the growth rate over the size intervals in order to get the single value which will be compared to the values determined with the methods. This is now made clearer and the paragraph now reads:

> **The condensational growth rates in the simulations, GR_{sim}, were ambiguous, since in the growth rate scenarios 2 and 3 charged particles grew more rapidly than the neutral ones, and also because in the scenarios 4 and 5 all the particles grew with a diameter-dependent rate. Furthermore, the division of the particles into the size sections in the model resulted in a small error in the condensational growth rate of the particles in all of the simulations (Leppä et al., 2011). Since the iteration and fitting methods provide two estimates on the value of GR for each simulation (one for DR1 and the other for DR2), we needed to estimate the corresponding values of GR_{sim} in order to compare the values determined with the methods to those observed in the simulations. When estimating the value of GR_{sim}, the growth rates of neutral and charged particles were weighted with the fractions of neutral and charged particles, respectively, and the effect of numerical error was estimated**

according to equations presented by Leppä et al. (2011). The values of GR_{sim} for DR1 (DR2) was then estimated to be the average growth rate of the particles during their growth from 2.2 (3.0) to 11.5 nm in diameter. As a result, we obtained two values of the growth rate for every simulation: one to be compared to the estimated growth rates obtained using data points in DR 1 and the other to be compared to the estimated growth rates obtained using data points in DR 2.

3. p. 21897, l. 11 – 12: How is possible to have the ratio of the initial charged fraction to the fraction of IIN be greater than 1?

Here the initial charged fraction is the one determined with either the fitting or the iteration method, which is now clarified in the text (reproduced below). Though the methods may overestimate the fraction of IIN, the initial charged fraction may exceed the fraction of IIN in ambient conditions only if the removal rate of neutral particles would be greater than that of the charged ones.

The ratio of the initial charged fraction determined with either the fitting or the iteration method to the fraction of IIN used as input in the model varied between 0.36 and 1.43, excluding the situations with small fraction of IIN (< 0.5 %) or too small growth rate.

Technical corrections:

1. p. 21869, l. 12: Consider replacing "big" with "large", when indicating relative size here, and in subsequent instances.

Changes were made according to the suggestion.

2. p. 21869, l. 13: Amend to read "By activation, we mean a process by which the ion reaches a size…"

Text was changed according to the suggestion.

3. p. 21869, l. 23: Amend to read "is important from a climate change…"

Text was changed according to the suggestion.

4. p. 21870, l. 1: Amend to read "particles are at a balance…"

Text was changed according to the suggestion.

5. p. 21871, l. 8: Amend to read "…we aim to address the effect of the following conditions on the precision…"

Text was changed according to the suggestion.

6. p. 21872, l. 8: Amend to read "…in a case of a non-growing…"

Text was changed according to the suggestion.

7. p. 21872, l. 17: Amend to read "…as the ratio of the fraction…"

Text was changed according to the suggestion.

8. p. 21877, l. 15: Amend to read "instrumentation"

Text was changed according to the suggestion.

9. p. 21877, l. 17 – 18: Amend to read "…rates higher than the largest value…have been observed…"

Text was changed according to the suggestion.

10. p. 21882, l. 14: Amend to read "fraction at 1.8 nm in diameter."

Text was changed according to the suggestion.

11. p. 21885, l. 17: Amend to read "…and due to the fact that…"

Text was changed according to the suggestion.

12. p. 21893, l. 14: Consider replacing "things" with "aspects"

Text was changed according to the suggestion.

13. p. 21893, l. 15: Amend to read "…has to be sufficiently high, preferably at least…"

Text was changed according to the suggestion.

14. p. 21897, l. 23: Amend to read "…a value indicative of charge equilibrium…"

Text was changed according to the suggestion.

15. p. 21914, Table 5 caption: The units of the new particle formation rate should be 1cm-3 s-1.

Corrected.

16. p. 21922, Figure 8 caption: For the sake of clarity, amend to read "…initial charged fractions on the y-axis (A and B) are determined…"

The caption of Figure 8 was clarified and it now reads:

> **As Fig. 7, except that the initial charged fractions on the y-axis of panels A and B are determined using the fitting method, instead of the iteration method, and the cumulative frequencies of occurrence shown in panels C and D are changed accordingly.**

Anonymous Referee #3
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In this manuscript the authors tested the applicability of several data analysis methods to determine the growth rate and the proportion of ion-induced nucleation from the measured charged fractions. The approach is to compare the growth rate and initial fraction of charged particles estimated from these methods with the values obtained directly from the aerosol dynamic simulations. The authors found that the accuracy of the data analysis methods depends on a number of factors, and concluded that the existing data analysis methods should not be used when the nuclei growth rate is less than ~3nm/h, or when charged particles grow much more rapidly than neutral ones. Measured charged fractions of freshly nucleated particles, if properly interpreted, can provide very useful insights about the mechanisms of new particle formation. The analysis and comparison presented in this study is useful to understand the applicability and uncertainty of the simplified data analysis methods. The following comments should be properly addressed before the publication of the manuscript in ACP.

1. In the last couple of years, quite different conclusions have been derived from the same measured charged fractions about the relative importance of ion-induced or mediated versus neutral nucleation processes: one based on simplified data analysis method (Laakso et al., 2007; Manninen et al., 2009; Gagné et al., 2010) and the other based on kinetic aerosol dynamic model (Yu and Turco, 2008, 2011). Does the study reported in this manuscript help to reconcile the difference?

This is a very good question. First of all, as shown already by Kerminen et al. (2007), the particle population bears memory of the initial charged fraction only up to a certain size which depends mainly on the particle diameter growth rate and concentrations of small ions. Depending on the diameter range of the measurements, the information of the initial charged fraction may be negligible in the measured charged fractions. In such cases, it is impossible to get information of the proportion of IIN by using neither simplified data analysis methods nor kinetic aerosol dynamics models. For this reason, in order to compare the conclusions on the importance of IIN obtained with the above mentioned methods, these methods should be used on a set of nucleation events, for which the growth rates are known to be sufficiently high. However, the comparison between the IIN used as input in the model and the initial charged fraction obtained using the iteration method, now given in the new Appendix A, does indicate that the methods tend to slightly underestimate the importance of IIN. A discussion on this matter is now presented in the Appendix A.

2. The simplified data analysis methods have been used to estimate the contribution of ion-induced or ion-mediated nucleation to new particle formation by the authors in a number of previous publications. Based on the new insights obtained in this study about the applicability and uncertainty of the simplified data analysis methods, please discuss the uncertainties in your previous estimation with regard to the contribution of ion nucleation to total particle formation. As you concluded, the method should not be used if growth rate is less than 3nm/h. According to Manninen et al. (2009), the median GR values for 1.3-3 nm “intermediate” ions at Hyytiälä in spring 2007 were estimated using ion mobility spectra to be ~1.9 nm/hr. Does this imply that you can’t apply the simplified data analysis methods to estimate the contribution of ion nucleation in a large fraction of nucleation event days observed at Hyytiälä?

Indeed, the high enough growth rate is essential for the iteration and fitting methods to provide reasonable estimates on the fraction of IIN and growth rate. According to Yli-Juuti et al. (2011), the median growth rates for 1.5-3, 3-7 and 7-20 nm particles at Hyytiälä were 1.9, 3.8 and 4.3 nm/h, respectively. Of the growth rate scenarios used in this study, these values correspond best with the scenario 4, in which the growth rate is increasing as a function of diameter. In the case GR scenario 4 and GR_{input} = 3 nm/h (GR_{input} = 6 nm/h), the growth rates for diameter ranges of 1.8-3, 3-7 and 7-20 nm are 1.3, 2.2 and 2.9 nm/h (2.6, 4.4 and 5.9 nm/h), respectively. In other words, the average growth rates at Hyytiälä are higher than in the case of GR_{input} = 3 nm/h, but smaller than in the case of GR_{input} = 6 nm/h, when the GR scenario 4 is used. In the case of growth rate scenario 4 and GR_{input} = 3 nm/h, the data analysis methods were not able to estimate the fraction of IIN when the data were taken from the size range of 3-11.5 nm. The reason for this was that most of the knowledge of the initial charged fraction had dissipated before the particles reached 3 nm in size, but there was no such problem in the case of GR_{input} = 6 nm/h (see Figure below). If the charged particles grow more rapidly than the neutral ones, the information prevails to

slightly larger sizes than in the case of growth rate being independent of the charge of the particles. As a conclusion, an average growth rate in Hyytiälä conditions is sufficiently high for these methods to be applicable. However, there are of course events with a growth rate smaller than the average value and in some of those cases the growth rate probably is not high enough. The applicability should be checked individually for each case, but it is beyond the scope of this study.

This aspect is discussed in the manuscript in Sect. 4.5.2, and the following sentence is added to the end of the fifth paragraph:

> **However, according to the observed variation in the growth rates, there are also nucleation events observed at Hyytiälä in which the growth rate is not sufficiently high for this information to exist at the sizes of DR 2.**

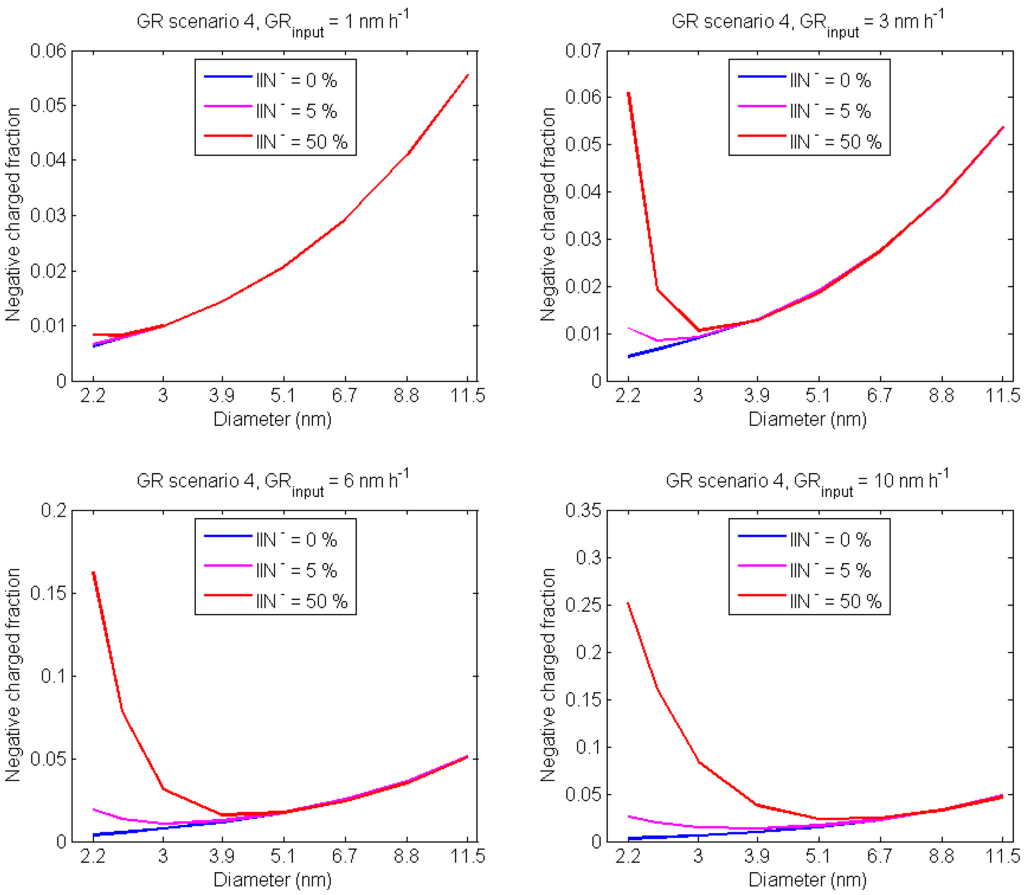

Figure that describes the loss of information of the initial charged fraction in the simulations with various growth rates and fractions of IIN used as input in the model.

3. Yu and Turco (2011) have discussed in detail the evolution of charged fractions of particles of different sizes based on a detailed size-resolved kinetic aerosol dynamic model. I am surprised

that Yu and Turco's work is not mentioned at all. It will be useful to compare the results of this study with those reported in Yu and Turco's work.

The purpose of this study is to test in which conditions the iteration and fitting methods are able to provide reasonable estimates on the proportion of IIN and growth rate of particles. In this regard, the work by Yu and Turco does not provide much. The discussion regarding the difference on the conclusions about the importance of IIN (see question and answer #1) is highly relevant though, and that has now been added.

4. This study uses results from aerosol dynamic simulations as references to assess the applicability of the simplified data analysis methods. What is the uncertainty of aerosol dynamic simulations? How much the uncertainty may affect the conclusions of this manuscript?

There are two kinds of uncertainties related to the simulations conducted in this study: (1) numerical issues that stem from imperfect description of the particle number size distribution and inexact analytical methods that are used to solve the equations governing the time evolution of the particle number size distribution and (2) physical issues that stem from imperfect and incomplete description of the physical processes governing the dynamics of the particles.

The most important numerical issues are the broadening of the particle number size distribution due to numerical diffusion and the underestimation of the particle diameter growth rate due to numerical diffusion and due to division of particles into size sections in a way that conserves the number concentration and volume concentration of the particles. The broadening of the size distribution affects the simulated charged fractions in the very beginning of the simulation. However, the data that the methods are used on is taken during the moment of the highest concentration of the size section (see Fig. 4 of the manuscript), in which case the broadening has negligible effect on the values of the charged fraction. The underestimation of the growth rate due to the division of particles into consecutive size sections is taken into account according to Leppä et al. (2011), as mentioned in Sect. 3.3. The underestimation of the growth rate due to numerical diffusion is not taken into account, but according to the results in Leppä et al. (2011), it is assumed to be of the order of ~3 %.

On the physical issues, we have no reason to believe that the model would lack any important process in context of this study. However, the model and iteration method use the same values for attachment and recombination coefficients, which may slightly improve the accuracy of the method when used on simulated data instead of measured data.

These uncertainties are highly unlikely to have considerable effect on the conclusions of this study, and hence they are not discussed in the manuscript.

5. P21869, Lines 11-20. What about ion-mediated nucleation (IMN) which includes IIN as well as the growth of neutral clusters formed by ion-ion recombination but are smaller than critical sizes?

In this study, the formation of particles and their subsequent growth to larger sizes are two separate processes. The particles are assumed to be formed with a diameter of 1.8 nm, which is larger than the diameter resulting from recombination of two small ions (details on small ions can be found in the answer to the comment #7). Thus, in the context of this study, it is important that, according to the current understanding, the particles can be formed neutral or carrying an electric charge. However, the specific mechanism of the formation of neutral particles, which can be clustering of neutral molecules or recombination of small ions for example, is irrelevant. For this reason, the part of the text referred to in this comment explains that the mechanisms that involve electric charges include IIN, but is not restricted to it.

6. P21869, Lines 19-25. Please give the values of the IIN fraction reported in this study. I agree that "The contribution of IIN to new particle formation is important from climate change point of view". In this regard, the different conclusions about the contribution of IIN or IMN to new particle formation derived from same set of observations (see comment 1 above) are highly relevant and should be discussed here.

The purpose of this study is to test in which conditions the iteration and fitting methods are able to provide reasonable estimates on the proportion of IIN and growth rate of particles. The proportions of negative and positive IIN used as input in the simulations conducted in this study are given in Table 1, with the total proportion varying from 0 to 100 %. Regarding this work's relevance to the different conclusions about the contribution of IIN or IMN see answer to the comment #1.

7. P21876, Lines 9-11. What are the sizes of small ions assumed in your model? How do you calculate the recombination coefficient of small ions with charged particles?

In this study, the electrical mobilities of negative and positive small ions were assumed to be 1.60 and 1.40 $cm^2\ V^{-1}\ s^{-1}$, respectively, which correspond to diameters of ~1.16 and ~1.24 nm, respectively (Ehn et al., 2011). This is now stated explicitly in the manuscript (Sect. 3.1, first paragraph).

The recombination coefficients between a small ion and an oppositely-charged particle are calculated according to Hõrrak et al. (1998). The equation used to calculate the recombination coefficient is given in the model description paper (Leppä et al., 2009), so it is not repeated in this manuscript.

8. P21886, Lines 14-21. Again the strong dependence of charged fractions on particle sizes has been illustrated in detail in Yu and Turco (2011). Are your results here consistent with those found in Yu and Turco?

The strong dependence of charged fraction and charging state on particle size is well known indeed (e.g. Kerminen et al., 2007 and also Yu and Turco, 2011). However, we are raising a slightly separate issue here. We are not considering the changes in the charged fraction as a function of size but the relation of the formation rate of charged particles (IIN) and the fraction of charged particles at the formation size. These two aspects are related, however, since they both depend on the condensational growth, coagulation and ion-aerosol attachment. The size dependence of the charged fraction depends also on the initial fraction of charged particles, but that is not the case here, except in the case of all particles being formed carrying a charge (Figure 2).

Other notable changes and corrections made to the manuscript:

The second paragraph of the Sect. 4.4.1 now reads:

> **Let us now have a more detailed look at the results belonging to the category 3. If the data points were taken from DR 2, the correspondence between $f_{ini,iter}^-$ and $f_{ini,sim}^-$ for results in category 3 was poor (Fig. 7). When charged particles grew more rapidly than neutral ones (GR scenarios 2 and 3), the iteration method tended to overestimate $f_{ini,sim}^-$ because the higher removal rate of charged than neutral particles due to the different growth rates was not taken into account. In other cases (GR scenarios 1, 4 and 5), the iteration method tended to underestimate $f_{ini,sim}^-$. However, if the data points were taken from DR 1, the correspondence between $f_{ini,iter}^-$ and $f_{ini,sim}^-$ for the results in category 3 was good, except for the overestimation of $f_{ini,sim}^-$ in the simulations in which GR scenario 2 or 3 was used and the underestimation of $f_{ini,sim}^-$ in the simulations in which GR scenario 4 was used. The underestimation in case of GR scenario 4 was mainly because the method assumed that the growth rate was constant with particle size, causing overestimation of the growth rate in the small sizes. For this reason, the charged fraction approached the value in the charge equilibrium less rapidly in the method than in the simulation, which resulted in an underestimation of the initial charged fraction when $f_{ini,sim}^-$ was higher than the corresponding value in the equilibrium.**

The colours of the data points in Fig. 7 were incorrect, which has now been corrected.

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