General Answer

The authors of this manuscript would like to thank both referees for their comments and questions. It has improved the readability of the manuscript as well as the quality of the analysis. We have further developed the methods. These developments touch two main points.

The first such point is the calculation of the diameter uncertainty. The calculation has been improved to include the DMA transfer function, the voltage applied to the DMA and the uncertainty on the flows inside the DMA. In the previous work, we calculated the uncertainty on both sides of the measured diameter but kept only the biggest of the two, that we used on both sides. Now we use each uncertainty measure on their respective sides. Hence, the referees will notice that the boxes in Figure 3 are no longer symmetrical.

The second point that has been modified is the generation of the randomized points within the uncertainty boxes during the fitting procedure. Those randomly generated points are now more constrained within the uncertainty boxes than they previously were. We believe that this is more representative of the measured data. This has also raised the standards for the evaluation of the fits' quality.

Finally, we would like to point out that, because of these changes, the average fraction of ion-induced nucleation is now 1.3 ± 0.4% compared to 0.8 ± 0.9%.. Note that these results overlap.

Anonymous Referee #1

General Comment

The authors implements previously-developed or still-developing methods for analyzing recent measurement data on the particle size distributions of electrically charged and total (charged + neutral) particles in 3-11 nm particle diameter range to learn about the contribution of ion-induced nucleation and also to verify whether it is possible to obtain diameter growth rates from measured electrically charged fraction of freshly nucleated particles in these size range. It is very meaningful that authors emphasize the effect of measurement uncertainty on the output of their theory-supported analysis. Their rural sampling site seems to be an ideal atmospheric environment for studying the dynamics of particle growth and particle-ion interaction occurring simultaneously under relatively small effect of scavenging by pre-existing larger particles and self-coagulation of nucleated particles and relatively high concentration of atmospheric ions. It is encouraged that authors continue accumulating data on this site since it is essential to have such data to verify any novel analysis technique suggested in this field. On the other hand, it is recommended that authors check the consistency of specific technical terms used in the paper before final submission.

A modified version of the Ion-DMPS is measuring at the Hyytiälä rural station now. The methods that have been used in this manuscript will be applied to that dataset in the near future. The method has been applied to a small selection of days to make sure it did not change the fraction of ion-induced nucleation significantly. It did not. The asymmetry is not as strong in Hyytiälä as it is in Helsinki but the small ion concentration is measured and available for most days. Applying these new methods to the rural background site measurements, in *overcharged situations promises to be very interesting.*

Regarding the technical terms, we realize that there is lack of a clear definitions, hence we have added a lexicon and modified the text consistently with those definitions.

Specific Comments

Is there a general agreement in the research field for the starting particle diameter (or critical size) of the IIN is 2 nm? Why not 1.5 nm or 1 nm? How significant the effect of chosen size on the conclusion made in this paper?

While we do not know exactly the size at which nucleation really occurs, it is thought to be somewhere between 1.5 and 2 nm. Although Laakso et al. (2007) presented the charging states at 1, 1.5 and 2 nm, and Gagné et al. (2008) at 1.5 and 2 nm, most recent studies present the fraction of ion-induced nucleation at 2 nm (see e.g. Manninen et al., 2010, Boulon et al., 2011). Those later studies, however, were performed using a NAIS. The ion-induced fraction cannot be retrieved from these instruments below the size of 2 nm. It should also be noted that final results from these studies are not directly comparable to studies performed with an Ion-DMPS because they also usually account for recombination of below-1.8 nm nanoparticles.

Moreover, since the submission of this manuscript, a new publication has appeared pointing out the importance of evaluating the fraction of ion-induced nucleation at 1.5 nm (Yu & Turco, 2011). To account for this demand, we ran the method LP (combining slopes and polarity asymmetry) at 1.5 nm and added the average fraction of ion-induced nucleation in Table 3, in section 3.2, and in the abstract. However, because of the lack of measurements at these sizes, the fittings are less constrained by the measurements and the results may be more uncertain.

Boulon, J., Sellegri, K., Hervo, M, Picard, D. Pichon, J.-M., Fréville, P. and Laj, P.: Investigation of nucleation events vertical extent: a long term study at two different altitude sites, Atmos. Chem. Phys., 11, 5625-5639, doi:10.5194/acp-11-5625-2011, 2011.

Gagné, S., Laakso, L., Petäjä, T., Kerminen, V.-M., and Kulmala, M.: Analysis of one year of Ion-DMPS data from the SMEAR II station, Finland, Tellus, 60B, 318–329, 2008.

Laakso, L., Gagné, S., Petäjä, T., Hirsikko, A., Aalto, P. P., Kulmala, M., and Kerminen, V.-M.: Detecting charging state of ultra-fine particles: instrumental development and ambient measurements, Atmos. Chem. Phys., 7, 1333–1345, doi:10.5194/acp-7-1333-2007, 2007.

Manninen, H. E., Nieminen, T., Asmi, E., Gagné, S., Häkkinen, S., Lehtipalo, K., Aalto, P., Vana, M., Mirme, A., Mirme, S., Hõrrak, U., Plass-Dülmer, C., Stange, G., Kiss, G., Hoffer, A., Törö, N., Moerman, M., Henzing, B., de Leeuw, G., Brinkenberg, M., Kouvarakis, G. N., Bougiatioti, A., Mihalopoulos, N., O'Dowd, C., Ceburnis, D., Arneth, A., Svenningsson, B., Swietlicki, E., Tarozzi, L., Decesari, S., Facchini, M. C., Birmili, W., Sonntag, A., Wiedensohler, *A., Boulon, J., Sellegri, K., Laj, P., Gysel, M., Bukowiecki, N., Weingartner, E., Wehrle, G., Laaksonen, A., Hamed, A., Joutsensaari, J., Petäjä, T., Kerminen, V.-M., and Kulmala, M.: EUCAARI ion spectrometer measurements at 12 European sites - analysis of new particle formation events, Atmos. Chem. Phys., 10, 7907–7927, doi:10.5194/acp-10-7907-2010, 2010.*

Yu, F. and Turco, R.: The size-dependent charge fraction of sub-3-nm particles as a key diagnostic of competitive nucleation mechanisms under atmospheric conditions, Atmos. Chem. Phys. Dicuss., 11, 11281-11309, doi:10.5194/acpd-11-11281-2011, 2011.

Page 15879, line 10. The method used to obtain GR from charged fraction in this paper is simpler than those used by Iida et al (2008). It may be inappropriate to state that the method was adapted from Iida et al (2008).

Yes, the method used here is a simplification of the method of Iida et al. (2008), for example, it neglects coagulation. Also, it is adapted to the Ion-DMPS which measures the charging state directly, while the method of Iida et al. (2008) measures particle concentrations. We replaced the sentence with this one:

"Finally, we use the behaviour of the charging state as a function of diameter to retrieve the growth rates, with a modified method of Iida et al. (2008). The version of the method used in this study does not include the effect of coagulation processes on the charging state, but it is adapted to work with or without the polarity symmetry assumption according to the derivation in Appendix A."

Page 15880, Line 1. The system used by Iida (2006) is based on a scanning mobility particle sizer (SMPS). It is not clear whether the DMPS operate under stepping mode or scanning mode.

The Ion-DMPS indeed operates in a stepping mode. We also realize that the description of the instrument and its products were not explained in a clear enough way. We expended and reorganized the description of the instrument in section 2.2:

"The Ion-DMPS (Laakso et al., 2007a, and also Mäkelä et al., 2003; Iida et al., 2006) is an instrument based on a Differential Mobility Particle Sizer (DMPS, Aalto et al., 2001) with the addition of a few modifications. A DMPS gives the size distribution of particles in time and selects the mobility equivalent diameter in a stepwise function. First, the particles are charged to a known distribution through a neutralizer, then the particles are size segregated by a Differential Mobility Analyzer (DMA, Winklmayr et al., 1991) and, finally, counted with a particle counter (CPC, TSI 3025, Stolzenburg and McMurry, 1991). Although the DMPS measures only charged particles, the concentrations are inverted to give the total particle concentration.

In the Ion-DMPS set-up, the neutralizer can be switched on or off, making it possible to measure the concentration of charged particles in ambient and in neutralized mode with the same diffusional losses. Since we are interested in their ratio, no inversion to calculate the total particle concentration takes place. Another difference with the DMPS is that the voltage in the DMA can be negative or positive, so that particles of both polarities can be detected. By combining these two modifications, the Ion-DMPS measures the size distribution in the 4 *modes: (1) ambient negatively charged particles, (2) neutralized negatively charged particles, (3) ambient positively charged particles and (4) neutralized positively charged particles."*

Page 15882, Line 1 to 14.
The third simple method a reader can easily think of is to calculate a representative charged fraction at a given size range by taking the ratio of average concentration of charged particles and total particles during an event period. This method integrates all the particle counts during the event period; therefore, it is the most noise-reducing method. In addition, a systematic uncertainty of the representative charged fraction can be calculated from the number of counts under ambient and neutralized modes. I imagine that authors chose not to take this simplest approach after long years of experience in the measurement of charged fractions, and the readers of this paper would like to know the reason.

The Ion-DMPS measures the concentration of charged particles at ambient and at equilibrium. It does not measure the concentration of total particles in any of its modes. The product is thus the charging state.

One major reason why we do not average the concentration of charged particles at ambient and the concentration of charged particles at equilibrium is that the charging state and the concentrations vary in time during an event, but not necessarily in a parallel way. If we really want to assess how much the charging state varies during an event, we should first calculate the charging state as a function of time, rather than to calculate the average concentrations and then derive the average charging state and its uncertainty. A short explanation was added: "In this case, taking the ratio of averaged concentrations would not allow for the evaluation the variability of the charging state."

Page 15882, Line 15 to 23
It is not clear whether the uncertainty mentioned in this paragraph is used as the value for the uncertainty box in the fitting procedure or not because descriptions here are not quantitative. In addition, the algorithm used to calculate the uncertainty of each method should be described more in detail. Readers would imagine that the uncertainty of the charged fraction of the first method is calculated from one standard deviation of the measured charged fraction. However, calculating in the uncertainty of the charged fraction of the second method is more involved. If authors have utilizing some statistical functions within a software to calculate the uncertainty of the slope they can refer to the function in the software. The uncertainty of the slope is most likely equivalent to the uncertainty of time-averaged charged fraction, which is different from the standard deviation among measured charged fraction by a factor of 1/(# of data)0.5. It is also helpful to mention here why MAD is chosen as a parameter to describe the scattering of the data.

This paragraph was rewritten to better describe the uncertainties and what they refer to. This section describes the uncertainty on the charging state at each diameter, and those uncertainties are used to draw the boxes around the measured points, before the fittings are done.

The uncertainty on the charging state when using the time average method is the standard deviation of the charging state during the NPF event.

The slopes method's uncertainty adds up the uncertainty on the concentration (of each point) using the derivative method and the squares of the perpendicular distance to the slope line. These are then divided by $(n-1)^2$ *where n is the number of points. No special software function is used in this case.*

"Each method has its own way of calculating uncertainties. The uncertainty of the diameter is common to both of them, and depends on flow fluctuations in the DMA as well as the DMA's transfer function and voltage input. The edges of the box correspond to the half-height of the theoretical transfer function that the classified particle has at a given diameter. The uncertainty of the charging state, however, is calculated in different manners depending on the method. In the time averaged method, the uncertainty of the charging state is the standard deviation of the charging state over time. In this case, taking the ratio of averaged concentrations would not allow for the evaluation the variability of the charging state. In the slope method, the uncertainty is the sum of the uncertainty of the concentration and the uncertainty attributable to the scatter around the linear fit."

The MAD, on the other hand, is used to represent the variation of the fitting results for each day. The Median Absolute Deviation shows how much the charging state S varies for one given nucleation event from one fitting to the other, using randomly normally distributed points around the measured points, inside the uncertainty boxes. The MAD is thus describing a variation, and differs from the quantities explained in this paragraph. We added this brief sentence in the text:

"The MAD is a value reflecting by how much the charging state varies from one fit to another due to measurement uncertainty (Gagné et al., 2008)."

Page 15884, Line 6-16
It is likely that most reader would find this paragraph too technical to understand. Which method (1 or 2) is being referred to by stating "charging ratio" in the first sentence? The last two sentences are especially unclear. What is the meaning of "median fit"?

We have rewritten this paragraph and tried to make it clearer. We also removed the lengthy explanations on why the conclusions are not affected. We also added the explanations regarding the new uncertainty calculations and randomization.

"In the work of Kerminen et al. (2007) and Gagné et al. (2008), the ion-induced nucleation fraction was estimated using the time averaged method. We have improved our uncertainty evaluation, which is described in section 2.3.1 as well as how constrained the randomly generated points fitted within the limits of the boxes. These modification reduced the magnitude of the MAD, but also the range within which the fits were made and, as a consequence, we could raise the quality standard's definitions described in section 3.2. These changes in the evaluation of the uncertainty do not have much effect on the values or charging state published in the above mentioned studies and they can still be trusted."

Section 2.3.3
I believe that most reader find the contents in this section confusing. It is recommended that author refine this paragraph to deliver important messages more concisely. Here are some points.

- Ion-DMPS only measures the f±. I believe that feq, which is needed to calculate S, is calculated using charging theory by assuming ion mobility, mass, and concentration are same between positive and negative ions.

As mentioned in the improved description of the Ion-DMPS, the instrument does not measure the fraction, it measures the charging state S. From the measured S, we can calculate the charged fraction f assuming that we know the equilibrium charged fraction f_{eq}. The actual f_{eq} is not used up to section 2.3.4 and is purely theoretical in section 2.3.3. However, in this work, we assume that f_{eq} is the one measured by Wiedensohler (1988) . We realize that this reference was missing and no mention was made of what we used for f_{eq}. We have now added this sentence in section 2.3.4 that mentions Wiedensohler (1988):

"To calculate the ion-induced nucleation fraction, we multiply the charging state S_0 of the event, obtained by fittings, by the equilibrium charged fraction f_{eq}. This gives the fraction of particles involved in nucleation that were charged at the diameter d_0. The equilibrium charged fraction used in this work is that given by Wiedensohler (1988). In the asymmetric case, the asymmetric charged fraction is used instead."

*Wiedensohler, A.: An approximation of the bipolar charge distribution for particles in the submicron*range, J. Aerosol Sci., 19, 387-389, 1988.

- The term f±asy is not well explained in words. I believe that f±asy are steady state charged fraction accounting for the difference in ion mobility, mass, and concentration between positive and negative ions.

Section 2.3.3 was rewritten, hopefully the Referee will find the new version better explained. The value of f_{asy} is not calculated from basic values, but rather scaled from the symmetric f_{eq} (as in Eq. 3). Because of this the mass of the ions is not of interest here. We have, however, decided to remove f_{asy} and merge it with f_{eq}. However f_{eq} is different in the symmetric and asymmetric case.

- The term f±eq is a confusing term because it accounts for difference in ion mobility and mass between positive and negative ions but not concentration. I think that author can explain about the analysis by using only f± and f±asy.

Yes, we re-wrote the text using only one variable for the equilibrium value in both the symmetrical and asymmetrical frameworks. This is now explained at the beginning of section 2.3.3, where we introduce a new f_{eq} in Eq. 3:

- In Section 2.3.2. K and S are free parameter why ion concentrations are needed.

The small ion concentrations are assumed to be the same for both polarities, in which case they do not affect the fitting of Eq. 1 to measured values of S. In a symmetric case, the small ion concentration is indeed not needed. The parameter K is free, and the concentration of *small ions in Eq. 2 comes from the derivation of the equation by Kerminen et al. (2007). When the ambient concentrations are not similar for oppositely charged small ions, we need the concentrations to scale the measured values of S before the fitting can be done.*

- I believe that one need to assume ion mass because ions masses are usually not measured at sampling site. However, I guess that ion mobility and concentration are measured by ion mobility spectrometer during most of the event days analyzed in this paper. It is not clear why ion concentration are taken from annual average values of BSMA .

The reason why an average had to be used is because the neither the BSMA nor any other ion spectrometer was measuring in Helsinki on the days that are analyzed in this work. This explanation is added at the end of section 2.3.3.

"In this work, we used more than one year average of small ion concentration measured with a Balance Scanning Mobility Analyzer (BSMA) (Tammet, 2006). The need for an average stems from the fact that no ion spectrometers were measuring in Helsinki during the measurement period of the Ion-DMPS."

Page 15885-15886, Section 2.3.4.
Some reader may find it confusing that the value of S0 and K are separated into positive and negative in Table B1 & B3 since Section 2.3.2 says S0 and K are the two free parameters in the polarity-symmetry model. It may be more consistent with the assumption of the model if input charged fraction, steady state charged fraction, ion concentration, ion mobility and ion mass are all average values between positive and negative to make all the input parameter entirely symmetrical. Then solve equation (1) and obtain S0 and K. If S0 turned out to be close to average of Sasy+ and Sasy- the polarity-symmetry assumption is a good shortcut. Authors are free to decide either using current or above suggested approach.

The reader may be confused by the assumption used to develop the theoretical framework stating that the fraction of charged particles is the same for both polarities in the symmetric case. This assumption is only used to simplify the equations, and does not mean that in reality, the fractions really are the same. It is now stated in the text that this assumption is used only for theoretical purposes.

"In the case where we assume polarity symmetry, the charging state $S^{\pm}$ can be defined, for theoretical purposes, as the ratio of the ambient charged fraction ($f^{\pm}=N^{\pm}/N_{tot}$) to the neutralized charged fraction ($f_{eq}^{\pm} = \beta_0^{\pm}/\alpha$)."

In the symmetric case, the concentration of small ions, smaller than 1.8 nm, are about equal for both polarities. The symmetry or asymmetry of the small ion concentration defines the steady state charged fraction (f_{eq} according to Eq. 3). This does not imply that the nucleation process is to also be symmetric, but only that, in time, the particles will tend to the equilibrium f_{eq}. In reality, the value of S can be very different for each polarity for a same event day. This can be due to chemical affinity to condensing vapors, for example. Improvements in section 2.3.3 are hopefully making the matter clearer.

Page 15886, Line 16
It is more appropriate to state that "agreed well with GR_{PSD}" not "very well".

Okay, this was done.

Page 15886-7, Section 2.3.5.

Steady state charged fraction is non-linear function of Dp. If the measured f in some event days look non-linear function of Dp the author might have thought about applying a linear fit on a logarithmic scale, then express df/dDp in Equation 6 or 7 as (f/Dp)*(dlogf/dlogDp). It is not clear why authors chose to consider f is always a linear function of Dp.

This is an excellent point and we do not claim that the f is a linear function of dp. This confusion was caused by an earlier misinterpretation of the method developed by Iida et al. (2008). The correct way of using the method is now explained in the section 2.3.5 and we do not actually have to make any assumption on the diameter dependence of f.

In addition, Iida et al (2008) solved for f vs Dp by integrating the growth trajectory (Dp vs t) multiple times by adjusting GRf and until the solution fit with the measured f vs Dp; therefore, they did not obtain any slope by fitting because derivative taken from real data are sensitive to noises in the data. However, the approach taken by them was very time consuming.

This was also done in this version of the manuscript.

Ion concentration directly affects the solution of GRf, therefore, the ion concentration needs to be taken from the same NPF period during which Ion-DMPS was operating. It seems important to state in this paragraph that how the ion concentrations were selected as an input of this method.

Yes, the method would probably yield better results if we had access to the actual concentration of small ions for the same NPF event. Unfortunately, in Helsinki, we only have small ion measurements from different periods than the one covered with the Ion-DMPS.

In the polarity-asymmetry case (Eqn. 6) the difference in the values of ion-particle combination and recombination coefficients between positive and negative are not accounted.

The difference in the combination and recombination coefficients has been taken into account in the polarity-asymmetric case and the missing "±" marks are now added to Eqs. 8 and 9.

In Eqn 5 & 6 the ion-particle recombination coefficient is approximated by ion-ion recombination coefficient. Eqn 5 & 6 are still in the form of original rate expression under steady state; therefore, it does not seem necessary to apply any approximation in this equation. For example, ion-particle recombination coefficient in Eqn 5 can be calculated from the average ion property at each size.

This is very true. The recombination coefficients used in the analysis were calculated *according to parameterized version by Hõrrak et al. (2008) of the theory presented by Hoppel and Frick (1986). This is now stated in the end of section 2.3.5.*

Minor Comment

Page 15887, Line 15-16
The message of Figure 4 is very clear but the associated description in the text is not clear.

Yes, indeed. This is the caption now:
"Relative occurrence of event, non-event, undefined days (diamonds, circles and squares, respectively) as a function of the month of the year (percentage of measured days). The percentage of days without measurement is indicated by the no measurements line (crosses)."

15888 Line 15 & 16
The difference between Class-I(a) and Class-I(b) are not described.

According to Dal Maso et al. (2005) " Class I was divided into sub-classes Ia and Ib. Class Ia contains very clear and strong particle formation events, with little or no pre-existing particles obscuring the newly formed mode, making them suitable for modeling case studies of NPF events. Class Ib contains the rest of class I events." We now resume this difference in section 3.1.
"Class I are days for which the formation and growth rates can be determined with a good confidence level. Class I events are divided into two subclasses: Ia events that have high concentrations with little background concentration, suitable for modelling, all other class I events are in class Ib."

Figure 2. Units are missing. The axis title should be corrected to "concentration of charged particles".

Yes, this is now corrected.