Interactive comment on “Factors influencing the contribution of ion-induced nucleation in a boreal forest, Finland” by S. Gagné et al.

Anonymous Referee #3
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This article contains interesting experimental material on the role of ion-induced nucleation, as opposed to the nucleation of neutral molecular clusters. Important assets are the extensive data base and the various approaches used with regard to the data evaluation. The data and ideas are very much original, so that the paper appears suitable, after revisions, for publication in ACP. Several revisions, however, appear very necessary. My concerns and suggestions are outlined below.

A first general observation concerns the structure of the results Section 3. Here, the authors plunge into the results by showing a rather abstract Figure 1, which represents quite advanced yet abstract results obtained after much data processing. While the Figure itself is fine, it is a quite unfavorable start for a results section and should appear much later, i.e. when the reader has been faced in a more concrete manner with the experimental data. Once concrete examples have established a solid imagination of your data base, you can easily switch to the more complex and statistically-based results. Therefore, in view of the general importance of the article as well as the rich data base available I would appreciate to see a few selected case studies first, that help the reader to see clearly what is going on in terms of particle numbers (charged, noncharged), gaseous precursor and micro-meteorological parameters. Diurnal patterns of these parameters shown simultaneously in the same graph would help to see what is going on. In the conclusions, we can later read that “both ion-induced and neutral nucleation are taking place in the same event” albeit in different stages of the event evolution. I strongly assume that you may find some illustrative examples to support this conclusion from the beginning of the results section. This would help a reader appreciate that your conclusions are real.

Regarding the structure of the result section, we have made some changes that, we think, will help the reader to build a clearer image of the dataset. We added this text at the begining of section 3.1:

“The results presented in this section discuss the charging state of the particles i.e. which fraction of particles are charged compared to the charged fraction in the steady-state artificially created by an aerosol charger. The charging state varies in time and depending on the particle size. However, new particle formation events show characteristics of either more or less charges than the steady state at sizes close to where the nucleation occurs (around 2nm). Because of this, it is practical to present the results based on this classification (Gagné et al., 2008). In addition to these two relatively well-defined situations, more complex situations with altering charging state characteristics during the course of an event may also take place (Laakso et al., 2007b), but this is not covered in this work.”

We feel that adding examples from specific cases would only lengthen the manuscript without improving the readability. A few case studies would not help to understand what parameters influence on an event being overcharged or undercharged. For example, overcharged days happened on warmer days, however the diurnal variation of the temperature does not necessarily influence the fraction of ion-induced nucleation within a given new particle formation event.

Regarding the conclusion that ion-induced nucleation and neutral nucleation happen at the same time, this is already shown in figure 2a, where the fraction of ion-induced nucleation varies in time.This kind of behavior can also be seen from e.g. Laakso et al., 2007b (http://www.borenv.net/BER/pdfs/ber12/ber12-279.pdf), Fig. 4.

A second comment concerns the Section 2.2.1 (data classification). This section, which puts the shape and relevance of all subsequent results on the map, appears rather superficial, and remains only partly comprehensible for a reader even after studying the references Dal Maso et al. (2005) and Gagné et al. (2008) cited. To enhance traceability, and enable other researchers a comparison with their results, this section should be significantly expanded and clarified. Enhancement of this section is vital also in view of certain amounts of data having been removed from further analysis. See also comments below.

The section has already been improved after the comments of the two previous referees, especially in regard to the discarded days. The classification section 2.2.1 has been improved to describe the process better.
After the Dal Maso reference we added a short description:

"Event days were those when formation of 3-5 nm particles and their subsequent growth was observed. Non-event days were those when no formation and growth of new particles was observed. Undefined days were those that did not belong either to the event or the non-event class (e.g. either no growth, or no new particle formation was observed). The last class, called bad/no data took the days when the instrument was not working properly. Of these classified days, only the NPF event days were kept for analysis (event class)."

And after the Gagné reference, we added a short description:

"The classification was made by looking at the size distribution of the ambient and neutralized mode and comparing the concentrations of both, and this, for each polarity. The polarity and day was classified as overcharged if the concentrations of small particles was bigger in the ambient mode than in the neutralized mode; and as undercharged if they were smaller in the ambient mode than in the neutralized mode. It was classified as steady-state if both modes showed about the same concentrations."

Third, in Section 3 you often write about significant or insignificant differences in terms of aerosol and other atmospheric aerosol parameters between overcharged/ undercharged days. However, "significance" is not well defined in your article. Since this aspect of significance or insignificance of differences leads to the main conclusions of the article, it is advisable to introduce a quantitative measure whether the observed differences are of importance of not for the charging state of the nucleation particles. For instance, you could help yourself with statistical tests of various kinds. It would be great if a Table could summarize the results of such statistical tests, accompanying the text blocks in Section 3.2.

Yes, this is a good idea, we have performed t-tests on the temperature, the relative humidity and the global radiation. Those values are integrated in the text. And removed the terms "significant" and "insignificant" from places where it wasn't appropriate. All variables but the relative humidity showed a difference between over- and undercharged events at a 5% confidence level – that is the p-value<0.05. The relative humidity was still significantly different for both classes in the 10% confidence level. We integrated the numbers in the text rather than in a table, because the information is already included in the figures and including it in the text is less prone to misinterpretation. For example, for the temperature, we computed the temperature *anomaly, whereas for the nucleation mode particles, we used the peak of the time series. It is thus better to explain the meaning of the statistical tests in the text for each variable separatly. We however provide such a table here:*

	Overcharged median	*Undercharged median*	*p-value*	
Temperature	*0.23 celsius*	*-2.13 celsius*	*0.002*	*Seasonal difference*
Relative humidity	*-17.52%*	*-12.85%*	*0.104*	*Seasonal difference*
Global radiation	*64.73 Wm^{-2}*	*35.53 Wm^{-2}*	*0.001*	*Seasonal difference*
Nucl. mode ptcls.	*1.1e+3*	*1.5e+3*	*0.033*	*Median during the event period*
Sulph. acid sat. ratio	*1.9e-3*	*4.3e-3*	*0.019*	*excluding summer months (log of sat ratio)*
Sulph. acid sat. ratio	*1.2e-3*	*3.9e-3*	*0.0002*	*including summer months (log of sat ratio)*

Actually, this exercise allowed us to discover a minor problem in our code and so figure 6 is slightly changed. We also adjusted the text accordingly.

Fourth, your interest is focussed on the charging state of nucleation mode particles. I would also be curious to learn about differences in the concentrations of charged/noncharged particles in the bigger size ranges? Do they correspond to what we expect, i.e. how close are they to Boltzmann's charge equilibrium? In the conclusions, I am also missing a statement on how relevant ion-induced nucleation might be, after all, in the boundary layer. How much is it likely to contribute to the average number of 3, 10 nm particles?

The particles reach the steady-state as they grow. For example, in Hyytiälä, they usually reach the steady-state charged fraction already before 7nm (see for example Kerminen et al., 2007 figures 2, 3, 4, 5, 9 and 10 or Laakso et al., 2007a (http://www.atmos-chem-phys.net/7/1333/2007/acp-7-1333-2007.pdf) figures 3, 5, 6 and 8).

Ion-induced nucleation is, according to the results of Laakso et al., 2007a, Gagné et al., 2008 and Manninen et al., 2009a, responsible for between 6 to 10% of the boundary layer new particle formation. How much of these newly formed particles survive to grow until 3 or 10nm can be roughly estimated from equation # 14 of Kerminen & Kulmala, 2002. However, if 10% of 2 nm particles are produced through ion-induced nucleation, 10% of the 3 and 10 nm particles are likely to be from the same particles, even though the nucleation rate at larger diameters is smaller. This could change of course if the neutral and charged particles are scavenged at different rates. However, the charged particles recombine early (at small sizes) and become neutral. Studying the scavenging of charged particles compared to neutral ones would be a subject for a publication on its own. Boy et al., 2008 estimated the contribution of IIN in the boundary layer for 3-10 nm particles to be "up to 15%". This was added in the introduction since it is not a direct conclusion of our study, but rather describes its *importance in the big picture.*

“Based on measurements in Hyytiälä, Finland, Boy et al., 2008 estimated the contribution of ion-induced nucleation to 3-10 nm particles in the boundary layer to be up to 15%.”

Boy, M., Kazil, J., Lovejoy, E.R., Guenther, A. And Kulmala, M.: Relevance of ion-induced nucleation of sulfuric acid and water in the lower troposphere over the boreal forest at northern latitudes, Atmos. Res., 9, 151-158.

Detailed comments:
“overcharged days”, “undercharged days”: these terms sounds very much like technical jargon at the very beginning of the abstract. Define these terms first, and reformulate in a more general language.

Yes, we modified the abstract to make it easier to understand:

“We show that the classification into overcharged (implying some participation of ion-induced nucleation) and undercharged (implying no or very little participation of ion-induced nucleation) days, based on Ion-DMPS measurements, agrees with the fraction of ion-induced nucleation based on NAIS measurements. Those classes are based on the ratio of ambient charged particle to steady-state charged particle concentration, known as the charging state.”

p. 25804, l.11: bipolar charger can be “switched on and off”. A radioactive charger cannot be switched on and off, it’s always “on”. Probably you want to say something like “the bipolar charger can be bypassed”, or “aerosol samples can be conducted either passing through or around the bipolar charger”.

The charger in the Ion-DMPS is constructed in such a way that the radioactive source turns so that it is shielded or not, so basically there is no "bypass" and the samples all pass through the same inlet system. This construction was carefully planned to reduce any artificial bias.

p. 25804, l.23: “when the charging state is smaller than the one”: sentence hard to understand.

Yes, we added one sentence to clarify the meaning of the charging state and make it more clear that the charging state is a ratio and thus 1 means equality between the numerator and denominator. Also we changed the punctuation.

“The charging state is defined as the ratio of the ambient charged particle concentration to its corresponding neutralized (charge steady-state) concentration. Hence the charging state is the ratio of the fraction of charged particles in the ambient sample to the fraction of charged particles in the neutralized sample. When the value of the charging state is larger than one (i.e. when there are more charged particles in the ambient air than there are at the steady-state), the particle population is said to be overcharged. Oppositely, when the it is smaller than one (i.e. when there are fewer charged particles in the ambient air than there are at the steady-state), the particle population is said to be undercharged. Alternatively, if the it stays around one, the particle population is said to be at the steady-state charging.”

Section 2.2.1, data classification This section is the part of the paper that essentially defines the data set and subsequent analyses. However, it appears quite superficial in its present form. The methods of event selection and classification are drafted only very briefly, although they are necessary, for instance, for other researchers to compare the results quantitatively with their own work. In summary, I recommend the entire section to be expanded and clarified. If necessary, Figures could be added to illustrate and oppose clear and ambiguous cases of charged, undercharged, and steady-state events.

Yes, we clarified this section (see answer to earlier comment #2 and the modifications made from after the first two referees).

"loosely based on the classification of Dal Maso et al. (2005)": Even if the classification is only "loosely based" on the previous work, some sentences should be added to clarify the procedure itself to the more ingenuous reader, and illustrate the differences to Dal Maso's work, particularly when event frequencies are compared.
Yes, see answer to earlier comment #2.

p. 25811:, l. 16: "thermodynamic principles": What are these principles and how do they relate to the present results?
Kulmala et al., 2007 state that "When the saturation ratio is increased above a certain limit by increasing the T in a CPC, ion clusters will be activated first.". *Another appropriate reference would be Winkler et al., 2008. It says that charged particles activate with a lower saturation ratio than the neutral particles, so more easily. A sentence explaining the basic principle was added so that the reader does not need to get the paper to understand the connection.*
"[...] agreement with the thermodynamic principle described in Kulmala et al., 2007b and observed by Winkler et al., 2008 according to which charged particles activate with a smaller saturation ratio than neutral particles."

p. 25811:, l. 20 and Figure 2b: "the agreement is good". How do you arrive at this conclusion? Sincerely, I wouldn't call differences by a factor up to five in both directions a "good agreement". It might be advisable to add bars of uncertainty to the data points and scrutinize the reason for the many "outliers". In fact, this comparison suggests that one of the methods to determine growth rates is questionable.
Yes, we added some additional precisions about the weaknesses of both methods, also we removed the statement that the agreement is good.

"In general, both methods showed a similar tendency. There were, however, a few points with especially large ion-induced fractions for only one of the methods. Both methods have their strengths and weaknesses. While the extrapolation method is sensitive to uncertainties in Ion-DMPS measurements and requires well-behaved data points. It usually gives a good idea on whether the event is over- or undercharged. The method based on NAIS measurements is most inaccurate when the value of J_{ion} approaches that of J_{tot} or when J_{tot} is small. Due to different reasons causing uncertainties in determining the ion-induced fraction had with these two methods, it is not surprising that we have a few extreme points in Fig. 2b. Once these outliers are removed, the NAIS with its formation rate ratio compares fairly well with the charging state extrapolation method applied to the Ion-DMPS measurements."

"External radiation": If the external radiation considered is gamma radiation, why not calling Section 3.2.4 "Gamma radiation"?
The authors would prefer not to change that term because it was defined that way several years ago and refered as such in the relevant literature (e.g. Hatakka et al., 1998). External radiation includes cosmic rays, gamma radiation from the soil and from airborne radionuclides.

Section 3.2.5 "Growth rates" The results are only briefly stated. What I am missing here is some discussion about what your findings are relevant for, and whether they are in line with theoretical expectations.

We answer on the relevance of the finding in this paragraph:

"The fact that growth rates were bigger on undercharged days has another implication when considering the work by Kerminen et al. (2007). They developed a method to extrapolate the charging state (that is how charged the particle population is compared to the equivalent steady-state population) to smaller sizes from Ion-DMPS data. This extrapolation method is valid only if the information about the charging state is preserved until the detection size (3nm). This is the case when the nuclei grow fast enough. If the nuclei growth rate is low, information about the original charging state will be lost before the particles reach detectable sizes. This means that if undercharged days generally had higher growth rates than overcharged days, it is unlikely that undercharged days had in reality been overcharged days for which the memory had been lost."

Also, Iida et al., 2008 use the charging state to estimate growth rates from new particle formation days in Mexico city.

Fig. 2b, caption "Ion induced fraction" of what? Sloppy language, should be improved stylistically.

Yes, we changed the first sentence of the caption like this:
"Fraction of ion-induced nucleation as a function of the time after sunrise."

Sect. 3 "when the events are going on" "a bit below 10 ion pairs" (exactly?) "simple" (simplistic)

Yes, we changed "when the events are going on" with "the period during which the newly formed particles appear";

"a bit below 10 ion pairs": we changed the sentence to include the 25th and 75th percentiles, as well as the median: "The median ion pair production rate due to gamma radiation was around 9.1 ion pairs s^{-1} cm^{-3} (25th and 75th percentile around 6.0 and 9.6 ion pairs s^{-1} cm^{-3} resp.) and for undercharged days, and it was around 9.7 ion pairs s^{-1} cm^{-3} (25th and 75th percentile around 9.3 and 10.3 ion pairs s^{-1} cm^{-3} resp.) for overcharged days.";

"simple" was kept as is, the calculations are not simplistic, but they are not complicated or extremely detailed.

Sect. 5 "steal away" "perhaps"

Yes, we replace "steal away" by "monopolize";

"is perhaps due" by "may be due";

"perhaps the difference in sulfuric acid availability play a part in this phenomenon." becomes "the sulfuric acid difference may be playing a part in this phenomenon."