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Atmospheric
Chemistry
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Discussions

Interactive comment on “Detecting charging state of ultra-fine particles: instrumental development and ambient measurements” *by* L. Laakso et al.

L. Laakso et al.

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The authors would like to thank referee for critical comments, which improved the manuscript considerably.

Page 6402 Page 6402, lines 5-7. Concerning the following sentence in Abstract: “We performed several laboratory tests to test the operation of the device and then we measured atmospheric new particle formation events with the instrument in a boreal forest”. Probably the “events” were not measured, but the naturally and bipolar charged particle size distributions in a certain size range.

Corrected

Page 6402, lines 9-11. Concerning the following sentence in Abstract: “We also found that negative and positive ions behaved in a different manner, days with negative over-

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charging were more frequent than days with positive overcharging". Here it is rather unclear what the authors mean with the term "ions". I am also concerned about the terms "negative overcharging" and "positive overcharging". In the case of bipolar charging/neutralization the process (charging) cannot result in "overcharge" on particles, but only the steady-state charge distribution on particles. Due to the contribution of ion-induced nucleation, the particle population can be considered as overcharged compared to the steady-state charge distribution. The latter (overcharged state) is not due to charging, but due to the condensation of vapors around the cluster ions. Therefore, the use of a still undefined term "overcharging" is probably not correct in Abstract.

Clarified terminology.

Also, the last sentence in the Abstact (lines 12-13) is trivial.

The authors do not agree with this comment.

Page 6403. Insufficient credit is given to the earlier works in Introduction, e.g. by Laakso et al. (2004), Vana et al. (2006). The authors should summarize the results of their earlier works.

Some text + reference added

Page 6403, lines 5-7. Ion spectrometers are certainly not the "recent development".

Text somewhat changed. Also references to relevant papers by Misaki are included.

Page 6403, line 11, instead of "chosen" we recommend the using of "separated". Page 6403, line 25. I recommend the adding of the concretization "on particles" just after the "electric charges".

Added

Page 6403, lines 26-28. Comment regarding the sentence: "In case of ion-induced nucleation, new particles are formed electrically charged, whereas in case of neutral nucleation particles do not initially carry any charges". The statement is not entirely correct, because the small ion recombination, which is also considered as a new particle formation mechanism by ion-induced (or ion-mediated) nucleation (Turco et al., 1998), can result in the formation of neutral stable particles as well.

Ion-ion recombination takes always place in the atmosphere. In many cases it will lead to neutral clusters. If nucleation on such clusters is ion-induced nucleation is a matter of definition. We use ion-induced nucleation for the cases where particles that start to grow carry electric charge. We also try to be moderate: we do not want to explain everything with ions, but we do not deny their importance either.

Several comments on Page 6404 were corrected according to suggestions.

Page 6405, lines 2-4. Regarding the sentence: "Given the maximum voltage, flow rates, and counting efficiency of the CPC, this corresponded to a size range approximately from 3 to 15nm in electrical mobility equivalent diameter".

Corrected and added DMA and flow rates added as suggested.

The bipolar charger (or neutralizer), which can be switched ON and OFF, is the only innovation in the ion-Dmps system, but unfortunately this innovation is not described in the paper. Thus, we recommend adding a principal scheme (or photos) of the bipolar charger, including dimensions and the following parameters: sample flow rate through the charger, residence time of particles in the charging zone and the concentration of polar charger ions. The data about the mean mobility of polar charger ions or mobility distribution is also highly recommended. Reading the caption of Fig. 1 I found that the aerosol sample is "either directed to the Differential Mobility Analyzer (DMA) via bipolar charger" or "the charger is bypassed". If there are two different pathways for naturally charged particles and artificially charged particles, then the losses can also be different. Therefore, a more detailed description of the bipolar charger/neutralizer of the ion-Dmps system is certainly needed to avoid misunderstandings in the interpretation of the results.

A better description of the charger construction was added to chapter 2.1: ”The charger is a rectangular brass construction, with dimensions of 100 mm, 27 mm and 15 mm for length, width and height, respectively. With the aerosol sample flow rate of 2.5 l min-1, the residence time inside the charger is approximately 1 second. A β-active Nickel-63 foil is attached to a turning cylinder on top of the charger body. The cylinder is attached to a stepper motor, which turns the foil either towards the sample flow (charger on) or facing the inside wall (charger off). The dimensions and activity is comparable to commercially available Krypton-85 neutralizers (TSI-3077A). The stopping distance in air for 946;-radiation from Ni-63 is considerably shorter than that for a Krypton-85, thus the Ni-63 effectively distributes its energy within the charger.”

Figure caption was clarified. There are only one path for both natural ions and charged particles.

In the section “2.1.1 Laboratory verification of Ion-DMPS”, the authors have described a lab setup for the generation of test aerosols. However, the description of the setup for the generation of ammonium sulphate particles is missing. Here I also recommend the presenting of some data concerning the sensitivity (the minimal concentration of ions in different size ranges, which can be reliable detected) and measurements uncertainty of the ion-Dmps.

Ammonium sulphate was generated from liquid solution. This is now pointed out in the text.

Minimal concentration is now addressed in section 2.1.3 Transport efficiency: “Assuming Poisson-counting statistics for the CPC and 15 second integration time this will lead to 42% and 13% relative error for concentrations of 0.1 cm-3 and for 1 cm-3, respectively. Due to this, concentrations below 0.1 cm-3 were neglected in the charging state estimations.”

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Page 6406 Page 6406, line 10. The diameter of the tube is missing.

In an ideal case losses due to diffusion in a laminar tube flow do not depend on diameter of the tube.

Page 6406, lines 11-13. Regarding the sentence: “In the ion-DMPS, the desired information is the ratio between the concentrations, which are exposed to the same losses despite their polarities or the number of charges”. First, I recommend the adding of a concretization “of particles measured in four different operation modes” just after the word “concentrations”.

Done

Second, I am concerned about the statement that “the concentrations are exposed to the same losses despite their polarities or the number of charges”. Did the authors estimated experimentally or theoretically the rate of diffusion losses of neutral and charged particles (3-15 nm), as well as the recombination/coagulation losses of charged particles in the inlet of ion-Dmps?

The number of particles and the residence times are that small that recombination and coagulation can not affect the results. Metal tubing is used to minimize charge accumulation to the sampling lines, which could increase losses of charged particles to the tube walls.

Page 6406, section 2.1.3 Charge balance and neutralization efficiency. The lab setup of these experiments is not well described. Should we assume here that in all experiments the setup was exactly the same as shown in Figure 1?

Transport efficiency and neutralization experiments were done with monodisperse silver particles, neutralization experiment to monodisperse silver and ammonium sulphate particles. This now more clearly presented in the text.

NB! Regarding the figure captions of Figures 2 and 3 (see pages 6420-6421). According to the paper text, there should be only one figure.

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Figure 2 now has upper and lower panels, as suggested by the referee. Figure number corrected accordingly.

Page 6406, lines 16-17. Concerning the sentence: “All the ratios were normalized with respect to the concentration of negative, non-neutralized particles”. It is not clear for the reader without reading the figure caption (Fig. 2), what are the ratios the authors mean here, why just the concentrations of negative, non-neutralized particles were selected for the normalization, how many lab measurements were done and how the normalization was done. We can only guess that the mean values of the concentrations of “non-neutralized particles” have been used for that purpose. By the way, the using of terminology “neutralized” and “non-neutralized” is not correct (it is even confusing) in the section “2.1.3 Charge balance and neutralization efficiency” and also in Figure 2 caption, because in lab experiments all the particles were neutralized by the first bipolar charger/neutralizer (see Fig. 1). So, in the lab the ion-Dmps measured neutralized or doubly neutralized particles. I have understood that under the terms “neutralized” and “non-neutralized” the authors mean the different operation modes of the ion-Dmps system, but it is not explained anywhere in the text in this section.

To test charge balance of the ion-DMPS charger, sampled polydisperse ammonium sulphate and silver with the ion-DMPS setup. To test ion-DMPS neutralizer efficiency, we generated a lot of monodisperse, negatively charged particles and subsequently examined, whether the charger of the ion-DMPS was able to neutralize them. We did the test only for negative particles, so we had to normalize the results with respect to negative, non-neutralized particles. As a result, the whole section is now reformulated and clarified.

Page 6406, lines 17-18. Is it correct to use the term “polydisperse particles” here? It is not clear for the reader whether the first DMA (see Figure 1) was also used in these lab experiments with test aerosols or not. Please add a comment in the text.

Modified, see above.

Page 6406, line 19. I recommend to specify, which one of the two chargers/neutralizers (see Fig.1) was switched ON by adding the term “ion-Dmps” just before the word “charger”.

Added

Page 4606 in line 20. The authors have estimated the increase in the concentration of sub-10 nm particles by approximately 10% after switching on the ion-Dmps charger compared to the corresponding “non-neutralized” negative particle concentration. However, in the Fig. 2 (upper panel), one can find the ratios above 1.1.

The average overestimation is approximately 10%, as stated. Ammonium sulphate ratios are substantially larger than 10%, but this is due to inability of the particle generation system to produce particles < 6nm from liquid solution. This is now pointed out in the text.

Page 4606 in lines 22-24. The authors have stated that the “Absolute concentrations were higher in the case of negative polarity. This is due to higher mobilities of negative cluster ions, which attach to the sampled particles in the ion-DMPS charger”. However, it seems to me that the differences more than 2 times in the positively charged particle (ion) concentrations compared to “non-neutralized” negative ones in Figure 2 is hard to explain by the differences in the charging efficiencies due to different mean mobilities of positive and negative small ions in the charger. Also, the latter parameters are not known for the charger used in the experiment. In accordance with the data given by Reischl et al. (1996), the ratio of positively to negatively charged particles (2-10 nm) in steady state conditions is about 0.6-0.7. Therefore, we have a reason to suppose that due to some unknown reason the positively charged particles had extra losses compared to negatively charged particles, or the concentrations of bipolar charger ions were significantly different.

See above, the whole section is re-organized and clarified. Our experiments agree with data with Reichl et al (1996) for particle size larger than 6 nm, for

both silver and ammonium sulphate. In this range, the ratio between positive and negative ratio is 0.6-0.7, but for smaller particles the ratio decreases. This is already pointed out in the text. Albeit being interesting and important, this topic is left for further study since it would need an extensive laboratory work.

Considering the output from ion-DMPS, the differences between polarities do not have a direct effect, since the overcharging is detected for both negative and positive side separately.

Page 6407 Page 6407, lines 8-11. Here the authors are using very approximate estimates like “higher than atmospheric concentrations” and “agreed well” to characterize the concentration of aerosol particles used in lab experiments to test the bipolar charger/neutralizer and the charge distribution on aerosol particles, respectively. I recommend to be more specific and to give some numerical estimates. Also, the authors have made conclusions about the functioning of the charger based only on negatively charged particles data (lines 10-12), but unfortunately forgot to give a comment about positively charged particles, which seem to deviate much from the parameterization given by Wiedensohler (1988) and Reischl (1996) (see Fig. 2). Also, the test of neutralization efficiency carried out is sufficient only if the chargers/neutralizers have similar characteristics.

It is true that positive charging deviated from experiments by Wiedensohler (1988) for smaller particle size. Note that neutralization experiment data is not in Figure 2 but a separate experiment. The authors feel that the purpose of this neutralization experiment related to this study is just a quality assurance that the charger is able neutralize high overcharging state to equilibrium conditions. A more detailed experiment would be a large enough task for a separate paper.

Page 6407, lines 13 and 15. According to Tammet (Tammet, 2004), the device used in measurements is called the Balanced Scanning Mobility Analyzer (BSMA).

Corrected

Page 6408 Page 6408, lines 5-8. The authors have not mentioned here that one of the ion-induced nucleation mechanisms, the small ion recombination, is also resulting in the production of neutral particles similarly as neutral nucleation. Unfortunately, the latter mechanism was not discussed in the paper at all.

As defined earlier, we consider ion-induced nucleation a process where particles are initially charged.

Page 6408, line 6. The correct reference is Fig. 4, second row. So, instead of “first row” there should be “, second row”. Page 6408, line 8. Similarly, instead of “Fig. 4, second row “ there should be “Fig. 4, first row”. Otherwise the figures in the first and second rows in Fig. 4 should be exchanged.

Corrected

Page 6408, line 21. Instead of “negative natural particles” I recommend using of naturally charged negative particles”. The particles measured in the field experiments are certainly natural, but the charges on particles can be natural or artificial (bipolar charger). Also, please indicate the size range of nanometer particles, where the concentration of naturally charged negative particles was higher.

That is visible in the subsequent figure.

Page 6408, line 23. The reference to figures (Fig. 5c and d) is not correct. The proper reference is “Fig. 5c and b, respectively” or “Fig. 5b and d, respectively” depending on the context the authors would like to point out.

Corrected

Page 6409, line 7. The term “neutralized ion concentration” is certainly incorrect here, the authors probably mean “the ion concentration after the neutralization of particles in the ion-Dmps”.

Clarified

Page 6409, line 8. The term “nucleation period” is not defined anywhere. Perhaps the “particle formation period” should be used instead of “nucleation period”.

Changed

Page 6409, line 10. Please consider the revision of the fragment “an overcharged nucleation event” using correct English.

Page 6409, line 13. Instead of “7 m particles” there should be “7 nm particles”.

Corrected both 2 above.

Page 6409, line 13. The authors stated that “the charging states of 5 nm and 7 nm particles are pretty constant”. However, in Figure 8 we can see that the ratio can vary from values close to zero up to about 2-3. As no uncertainty estimates have been given, nobody can realize whether these changes (variations) are within instrumental uncertainties or whether they have also some physical background.

This text is referring to figure 7. The figure 8 considers all the new particle formation event days. During some of the days event the larger (5-7 nm) are highly overcharged.

Page 6409, last paragraph (lines 21-23). The authors inform the reader about the testing of the ion-Dmps with test aerosols (ammonium sulphate particles) during the field campaign. However, the results of the ion-Dmps tests are not discussed anywhere in the paper.

Field verification yielded same information as the lab-calibrations. This is now explicitly stated.

Page 6410 Page 6410, lines 11-13. Regarding the sentence: “One must remember, however, that the charging state of sub-5nm particles could not be determined during the non-event days due to absence of these particles from the measured size spectra”.

Concentration limits for the accepted data is now presented under instrumenta-

tion and transport efficiency.

Page 6410, line 22. The derivation of Equation 1 from the analytical formulae given by Kerminen and Kulmala (2002) is not straightforward. The latter formula was derived assuming neutral particles. Taking into account also the charging/neutralization processes, the particles can be as in neutral as in charged state during the growth. In principle, the growth rate for neutral and charged clusters and nanometer particles can be different. The growth rate is also one of the parameters in the analytical formulae given by Kerminen and Kulmala (2002), but its value (or values) used in the present model remains unknown. So, more information is needed to explain the derivation of the Equation 1. Also, the accuracy of Eq. (1), as well as its sensitivity to input parameters are not discussed in the paper, for example, the uncertainty due to neglecting the size dependence of the ion-aerosol attachment coefficients. The attachment coefficients for the charging of neutral particles are increasing about 5-6 times if to compare 3 nm particles with 10 nm particles. In the present model it is assumed as a constant, but its value (or corresponding particle size) also remains unknown.

We totally agree with this comment. Motivated by this, and the similar comment by the other reviewer, we made a more detailed theoretical investigation on the behavior of the nuclei charging state. Most importantly, we re-derived equation (1) without making the wrong assumption that ion-aerosol attachment coefficient is constant with particle size. As a result, the new equation (1) is different from the one presented in our previous version of the manuscript.

Describing the derivation of equation (1), including investigating its validity under different atmospheric conditions, takes more than 10 journal pages, so we decided to present it in a separate paper that will be submitted to a journal in a near term (Kerminen et al. 2007).

Page 6411 Page 6411, line 25. The order of magnitude of uncertainty estimates should be given for the average contribution of ion-induced nucleation to the total new particle formation rate.

As a result of re-deriving equation (1), we totally rewrote sections 4.1 and 4.2 and combined them together. Uncertainties were better taken into account when presenting the results, especially with regard to the contribution of ion-induced nucleation.

Page 6411, line 22 and 28. Instead of “over charging” should be “overcharging” or “overcharging rate”.

Page 6412 Page 6412, line 21. The reference to paper by Hirsikko et al. (2005) is probably not correct.

Page 6413 Page 6413, line 7. Instead of “device” should be “divide”.

Corrected all 3 above.

Page 6413, second paragraph (lines 4-12). It is not clear why the model results about the contribution of ion-induced nucleation to the total new particle formation rate should be divided by a factor 3. If this is due to the fact that the maximum contribution should be 100%, but the model gives the maximum of 300%, then such a rough approach is certainly not correct, because the uncertainty estimates of the model are rather qualitative than quantitative.

After re-deriving equation 1, and rewriting sections 4.1 and 4.2 this comment is of no concern any more.

Page 6413, third paragraph (lines 14-17). Here I recommend indicating also the mobility/size range of particles used for the fitting of data points.

Clarified

Page 6413, last paragraph (lines 25-27) and Page 6414, first paragraph (lines 1-3). It should be kept in mind that much time (hours) is needed for the charging of nanometer size particles in the atmosphere (due to low charging probability) to reach the situation close to steady state condition. So, I guess that in atmospheric conditions the negative slope in the mobility/size distribution of ions above 2 nm due to neutral nucleation is mostly improbable.

No changes needed

Page 6413, line 27. Instead of “part of particles are charged” should be “minor part of particles get charged”, otherwise the sentence is not correct.

Not changed

Page 6414 Page 6414, Cases 2 and 3 (lines 4-7). To draw any conclusions about the nucleation mechanism, it should be kept in mind that the charging of initially neutral particles in the atmosphere to obtain the steady state charge distribution on particles is many times slower process (more time consuming) than discharging of charged particles (ions). Thus, the residence time of new particles in the atmosphere before the measuring should be known.

As pointed out by the referee, more exact estimates on relative roles of ion-and neutral nucleation in boreal forest would require more precise knowledge on the timescale of growth of newly formed particles to Ion-DMPS size range. This is addressed partly in the derived equation by Kerminen et al. 2007.

Page 6414, lines 14-16. Regarding the following sentence: “Some of the days were clearly overcharged which indicates contribution of ion-induced nucleation on new particle formation whereas some days were undercharged and thus neutral nucleation dominates”. The days cannot be overcharged or undercharged, but the charging state of particles can be considered as overcharged or undercharged compared to the steady state charge distribution.

Corrected

Page 6414, line 22. Comment on contribution of ion-induced nucleation to total nucleation rate.

More exact estimates on relative roles of ion-and neutral nucleation in boreal forest would, however, require more precise knowledge on the growth rate of newly formed particles to Ion-DMPS size range. This is now included in the conclusions, as suggested by the referee.

Page 6414, lines 22-23. Regarding the following sentence: “Minimum contribution was found to be close to 0% and maximum close to 100%”. This result is trivial and can be concluded without any measurements, and, therefore, it is recommended to be dropped out from the conclusions.

The authors want to stress that these results indicate that during some of the days that contribution of ion-induced nucleation on new particle formation is significant, whereas some days were undercharged and thus neutral nucleation dominates. See also comment above.

Page 6418, Table 1. The heading of Table is not as informative as it should be. and related comments.

Table caption is amended. Table now includes new fitting parameters and estimated upper and lower limits. The fitted function has a form derived by Kerminen et al. 2007 and presented in the manuscript as equation 1.

Page 6419, Figure 1. In figure caption (line 5) I recommend the using of “measurements of ion concentration of both negative and positive polarities” instead of “measurements of both negative and positive polarities”.

Added

Page 6420, Figure 2. It is not clear what is presented in Figure 2.

Figure caption corrected and shortened. The discussion is now within the text. Error bars depict variability from experiment to experiment (standard deviation).

Page 6421, Figure 3. Instead of Figure 3, there should be Figure 2, lower panel. In some cases there are two data-points with the same color label corresponding to a certain size of particles. What are these extra data-points? No explanation can be found in figure caption or in the paper text.

Extra data points represent data measured on a different day.

Page 6422, Figure 4. The meaning of the symbols “0” and “-1 or +1” in the left column is probably not clear for the reader and should be explained in the figure caption. Also, the “pink box” indicating the measuring range of ion-Dmps should be explained in the figure caption.

Clarified

Page 6424, Figure 6. The figure caption is not as informative as it should be. Also, the authors should explain in the paper text why the fitting does not follow the data-points above about 6 nm and the ratio is less than 1 (the particles are undercharged compared to equilibrium state) in the size range of 6-12 nm.

Figure 6 and 7 were completely re-drawn since new form of the fitted function.

Page 6425, Figure 7. Almost all the comments (excluding that of about the fitting and particles in the size range of 6-12 nm) can be found above.

See above.

Page 6426, Figure 8. Unfortunately, the time series of the ratio for positively charged particles is not indicated in the figure, but only one data-point.

Correct. We did not have negative particles. Also corrected errors in Figures 9, 10 and 11 according to referee suggestions.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 6401, 2006.