Review of manuscript acpd-14-171.2014: "Ion–particle interactions during particle formation and growth at a coniferous forest site in central Europe"

(submitted for publication in Atmos. Chem. Phys. by S. G. Gonser et al.)

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REFEREE REPORT

1 Overall assessment

I recommend the editor to accept the manuscript after minor revision.

2 Relevance

Investigation of new particle formation (NPF) has a long history. Early studies of this phenomenon can be traced back to the first half of the twentieth century. However, this phenomenon – occurring at about one-third of all days ('event days') – has still hitherto unexplained aspect, among others, regarding the role that ions might play in new particle formation. The present study aims at contributing to the elucidation of ion–particle interactions during NPF events at a coniferous forest site. The authors performed field studies employing state-of-the-art experimental equipment in combination with previously proposed evaluation and modelling tools. The key result is the empirical discovery that the abundance of nanometric particles is controlled by the formation of ions, which appear prior to the enhancement of the concentration of all nanometric particles ('total particle nucleation mode'). There is no doubt that the addressed problem is both interesting and of high relevance for atmospheric aerosol science.

3 Assessment according to criteria for ACP review and interactive discussion

1. Does the paper address relevant scientific questions within the scope of ACP?
   Yes.

2. Does the paper present novel concepts, ideas, tools, or data?
   Yes.

3. Are substantial conclusions reached?
   In parts (see specific comments).

4. Are the scientific methods and assumptions valid and clearly outlined?
   In parts not. Uncertainty analysis is incomplete (see specific comments).

5. Are the results sufficient to support the interpretations and conclusions?
   Only in parts due to missing sensitivity and uncertainty analysis (see specific comments).

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?
   I think it is impossible to trace back this comprehensive analysis (including the measurements) by some third party. It would deserve the experimental equipment, dedicated skills in using the employed tools, and a deep insight the details of the analysis. However, this point is not an argument to the disadvantage of the authors. Within the framework of an ACP paper the authors tried to make clear what they did or gave reference to previous studies.

7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution?
   Yes.

8. Does the title clearly reflect the contents of the paper?
   Yes.

9. Does the abstract provide a concise and complete summary?
   Yes.

10. Is the overall presentation well structured and clear?
    Yes.

11. Is the language fluent and precise?
    Yes.

12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?
    In general yes, for dimensional analysis of the expressions in the Appendix it would be helpful to add units to the symbols for 'mobility' quantities.

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?
    I think Section 'Discussion' can be condensed somewhat. All tables and figures are well prepared and explained.

14. Are the number and quality of references appropriate?
    Yes.

15. Is the amount and quality of supplementary material appropriate?
    No supplement included.

4 Specific comments

While the obtained result is already worth to be presented to the community, the presentation of the applied method deserves some polishing. Owing to the combination of primary measurements and model-based evaluation tools it is difficult to figure out

- what is a result of the measurements and what is a result of the applied assumptions for evaluation and modelling, and

- what are the uncertainty ranges of derived 'nucleation & growth' parameters at the lower range of detection.

With reference to previous studies the authors referred to a lower NAIS detection limit of 0.8 nm for atmospheric ions (page 174). This is a scale at which molecular and particle interactions become important. Their specification on the base of field measurements is very difficult, and it is probably that a major part of information is hidden in the uncertainty range of the measurements and evaluation tools. With regard to the law of error propagation theoretical work and modelling approaches to explain the discussed phenomenon should be guided by the declaration of empirical 'expectation ranges' rather than by information of mean or median values only. Without this information it is difficult (or even impossible) to realistically assess the progress reached by enhancement of the device performance and to quantify the predictive power of explaining modelling attempts.

Is it possible to quantify the uncertainty of the declared median growth and formation rates for 2-3 nm particles for total, negative, and positive particles, respectively (p. 182, Section 3.1) or the significance of the found differences? Is it realistic to expect 'explanation' of these differences by a model (at which level of uncertainty the phenomenon can be considered as 'explained')?

The same questions appear with respect to the explanation of the higher growth rate of 'total particles' as compared to the growth rate of ions only. The authors stated that total particles exhibited enhanced growth rates at diameters below 15 nm (in comparison to the growth rates of ions), and explained this phenomenon by enhanced ion loss rates leading to neutralisation of ions. Owing to the numerous assumption employed along the data evaluation it is difficult the assess the significance of this result. One can just say, it is possible but not compelling.

In the following I will try to give some specific comments, in the hope that they will be helpful for the authors. However, these are only recommendations which reflect my admittingly restricted view on the experimental aspects of the problem. The authors are welcome to criticise or reject my arguments.

- Page 173, line 9: The authors are asked to explain what 'total particles' are (unlucky notion). If charged particles are just a minor part of a particle ensemble, than it is understandable that changes in the whole particle ensemble can only be seen posterior to changes in some of the minor fractions (e.g., ions) with more or less pronounced retardation.

- Page 173, line 12: Please explain the notion 'overcharged' and 'equilibrium charging state' (see also line 23, and page 175, lines 19-24). This is nontrivial and essential for the topic of the study.

- Page 174, line 7: Radioactive decay and cosmic radiation are considered as the main source of sub-1.6 nm ionic clusters. As these processes do not have 'event-like' character, any burst-like behaviour of intermediate and large ions must be anyhow linked to growth or neutralisation processes. It would be helpful to add a critical assessment of the explanations given by previous studies (already cited in the text) on this finding.

- Page 175, line 4: Please add manufacturers information on uncertainties of NAIS.

- Page 176, line 17-28: The authors collocated a dataset by merging their NAIS data with data from the mobility particle size spectrometer by means of 'a linearly weighted merging algorithm'. Is it possible to add an example how this looks like? What about the total uncertainty of the resultant particle number size distribution between 2 and 680 nm underlying the calculation of the sink rates. Here, errors originating from different sources are superposed.

- Page 177, Section 2.2: The particle interactions (coagulation, ion attachment, recombination) have been 'calculated theoretically'. Here again, an uncertainty analysis would be helpful to span the corridor, inside which the 'true values' of the coefficients should be expected (maximum possible deviation from a reference value). Where do the authors get from, e.g., particle mechanic mobilities (please add unit), vdW interaction distance, or sticking probability? It is impossible to intuitively percept the overall uncertainties of the coagulation, attachment, and recombination coefficients in comparison to the corresponding size effect depicted in Fig. 1. The equality of the recombination and attachment rates was proposed in the section, but not depicted in Fig. 1. Instead, the authors referred to an 'approximated theory' by Hõrrak et al. (2008) etc. In view of the importance of the assigned parameters for the present approach, the *qualitative* description of the chosen approximations is, for my opinion, too fugacious here. The paper aims at elucidation of ion-particle interactions, an essential part of them is hidden in the underlying theory. Thus, the authors could add some additional sentences here.

- Pages 179-180, Section 2.3: I understand equation (1) balancing the number concentration of recombined particles, but I do not understand the 'ionisation rate' Q, which assumes that the 'ion production rate is a function of two ion sink terms only, the recombination and the attachment of ions to the present background aerosol' (see Eq.(A8)). If there would be no source of ions, then I would expect that the initially present ions in the atmosphere would have already been removed by the two sink processes. In contrast to this, one has Radon emission from the soil and CGR impacts, permanently creating new ions. What do you mean with 'ionisation rate' if there is no ionisation?

- Page 181, line 3: Again, the uncertainty problem. How the uncertainties in the method of Yli-Juuti et al. (2011) affect the conclusions drawn in the paper on

the growth process (growth of ions vs. growth of neutral particles)? Please try to quantify whatever is possible to quantify. The difficulty in the interpretation of the results is the indissoluble merging of measurements, semi-empirical evaluation methods, and model-based assumptions without accompanying uncertainty analysis for the rates of growth and particle formation.

- Pages 182, line 14: 'Soil gas' is a notion to describe the air volume in the soil, containing oxygen (allowing for respiration of both plant roots and soil organisms), and carbon dioxide as a respiration product of plant roots and soil microorganisms, and is not explicitly related to radioactivity. The unit $\mathrm{Bq\,m^{-3}}$ denotes the number of radioactive decay events per unit time and unit volume, but is not a 'gas concentration'. Please revise this sentence or make clear what is meant. Is 'Waldstein' a singular place with enhanced background radioactivity?

- Page 182, line 20, reference to Fig. 3: Radon is permanently emanating from the ground without diurnal variation. However, boundary layer mixing at a forest site is expected to reveal at least a weak diurnal cycle with suppressed mixing during night and enhanced mixing during the day. Hence, the radon concentration should reveal a dilution-induced minimum around noon. This supports author's conclusion regarding the link between radon and small-ions concentration pattern. The plotting of percentile regions in Fig. 3 is very fine in view of the very low concentrations observed. The large differences found between NAIS and AIS measured ion concentrations (the latter unfortunately not available for the same period) underline the high importance of an uncertainty analysis (page 183). The uncertainties in the measurement process (type A vs. type B device) are of the same order as the atmospheric effects we are looking for.

- Page 183, line 20: It seems that the authors have considered steady-state equilibrium between ion production and ion loss, which allows one to identify the loss rate with the production (ionisation) rate Q. Please make this clear at the place where the ionisation rate has been introduced. The authors derived a certain value of the ionisation rate, but at the same time suggesting that the true value is 'probably' a factor of three larger ... Maybe. It is experts suggestion, but its resilience is lower than that of calculated values.

- Pages 184-185, interpretation of Figure 6: Differences between the growth rates of ions and all particles can be seen, but their significance remains obscure. One should more carefully formulate (p. 185, line 3) that the '*derived* enhanced $\mathrm{GR_t}$ compared to charged particle growth rates stands in contrast to growth theories ...'. The notion 'observation' has a great 'authority' and 'reputation' which should be reserved for quality-assured measurements being subject of uncertainty analysis (JCGM 2008). In the present case different approaches (measurements, semiempirical approaches, balancing of uncertain source terms) have been mixed, which is of course justified, but softens the explanatory power of the conclusions. I cannot see any argument calling the cited growth theories into question, I only see that without a comprehensive uncertainty analysis it is impossible to draw conclusive statements about any molecular theory employed in the present modelling approach. Moreover, with respect to ion-particle interactions I consider it already as a very great challenge to

setup suitable laboratory experiments for their elucidation. The conditions in the field are much more difficult to control. It seems that at the level of nanoscale processes there are no pure 'observations', but the measurement process itself is already as complicated as the investigated atmospheric new particle formation. Thus, I suggest an 'equidistance' of both 'nanoscale observations' and 'nanoscale theories' to the 'nanoscale verity'. Perhaps, one should emphasise the tentative character of the present findings and modelling approaches and to be more carefully with respected to 'revision of theories' (an inappropriate modelling approach (by uncertain closure) does not necessarily imply a wrong theory).

- Page 186, line 17: There is no reason to expect that the evolution of the ion concentration can be explained only by condensational growth. The appropriate description of ion–ion and ion–particle interactions is a prerequisite for the closure of the time rate of change equation of the ion concentration. The correct tuning of these terms is purely empirical, a fortiori as in the paper the specification of the 'precursor gas' does not explicitly appear. Forward integration of a model and comparison with a predicted observable is very straightforward, but the derivation of a balance term from observed time series employing uncertain closure assumptions is not in equal measures.

- Section 4, Discussion: To my mind, this section can be shortened somewhat. Several points have been outlined previously in the manuscript.

5 Final comments

I found the study very interesting. The authors did a diligent work! If the authors cannot provide a comprehensive uncertainty analysis supporting their conclusions, I recommend to make the tentative character of the present findings more clear. In that sense, the revisions are minor.

(OH)

References

JCGM: Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement, Tech. rep., Joint Committee for Guides in Metrology, first edition September 2008, www.bipm.org, 2008.