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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Long-term observations of positive cluster ion concentration, sources and sinks at the high altitude site of the Puy de Dôme" *by* C. Rose et al.

Anonymous Referee #2

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General comments:

The authors have studied the balance of cluster ions in the atmosphere at the Puy de Dôme research station, located on the top of relatively high mountain (1465 m a.s.l.) in the Chaîne des Puys region of Massif Central in the south-central France. The behavior of cluster ions was investigated using five year dataset of air ion and aerosol particle measurements and applying a similar method as earlier used by Laakso et al. (2004) and Hõrrak et al. (2008). The aim of the study is to find out the sinks and sources responsible for the measured cluster ion concentrations during fair weather (clear sky) conditions at the Puy de Dôme station, concentrating on the differences in the behavior

of clusters ions during new particle formation event days and non-event days.

The present work by Rose et al. (2013) can be considered as one in the line of recent investigations of atmospheric ions and ionization rate carried out by Laakso et al. (2004), Tammet et al. (2006), Hirsikko et al. (2007a), Hõrrak et al. (2008), Schobesberger et al. (2009), Franchin (2009) and summarized by Hirsikko et al. (2011). The topic of the paper and the presented results are without any doubt relevant to the atmospheric scientists and worth to be published in the ACP. As far as I know this is the first time when the ionization rate (or cluster ion production rate) has been estimated for mountainous site, applying the balance equation of cluster ions and state-of-art measurement technique. However, the present manuscript still has some shortages, which should be satisfyingly resolved before it can be accepted for the publication in the ACP. The section 3.3.3 "Estimation of the ionization rate based on radon measurements" requires the most significant revision, as the gamma-radiation was not measured in this study and the estimates obtained from literature seemed to be inappropriate. All the figure captions and table headings should be more informative, including the data about measurement period and location.

The authors are asked to consider the following specific comments and recommendations to improve the manuscript.

Specific comments:

Starting with the introduction of the manuscript, I would recommend adding some relevant papers discussing the balance of small (cluster) ions in the atmosphere and the factors influencing it, namely the papers by Dhanorkar and Kamra (1994), Tammet et al. (2006), Hirsikko et al. (2007a) and Hirsikko et al. (2011), giving sufficient credit to the authors of these earlier works. Also works by Schobesberger et al. (2009) and Franchin (2009) are useful to mention in discussion. As the NAIS spectrometer, successor of the AIS, is mentioned in the introduction, I recommend also adding the reference to recent paper by Mirme and Mirme (2013).

In the beginning of the paper on Pages 14927-14941 the authors are discussing both the negative and positive cluster ion concentrations and their temporal variations, since the Page 14941 only positive cluster ions, as they have assumed that “positive cluster ions appeared to be more likely concerned by the NPF process”. The latter statement is not fully accepted, as Laakso et al. (2007), Wilhelm et al. (2004), Enghoff and Svensmark (2008) and many others have shown that negative charge preference on nanometer particles has been often found during the NPF events.

Also, reading the manuscript I felt that there is missing a table summarizing the statistics of cluster ions of positive and negative polarity. The graphical presentation of data (Figures 2-3 and 6) is not always enough to get an overview about the measurements and facilitate the general understanding of the results. Thus, it is recommend adding a table, e.g. into Section 3.2 Cluster ion concentration and size, which could be presented in similar form as Table 4 (in page 14962). If possible, this table might consist of data for both meteorological situations: clear sky conditions and cloudy conditions.

Sorry, but I did not understand, if not to take into account the title of manuscript, why the authors preferred not to present the characteristics of negative ions in figures, but use them only in discussion in the manuscript text. Comparison of negative cluster ion data with positive one could give some additional information for the reader, also support conclusions made based on positive ions.

Page 14930, lines 1-2 and lines 4-5. Please indicate the law of size-mobility conversion giving a proper reference.

Page 14931, Section 2.1 Measurement site. The Puy de Dôme station operated by OPGC/CNRSLaMP is certainly well known to the aerosol research community. However, in point of view of atmospheric electricity research some additional information should be provided, e.g. that the station is located on the top of relatively high mountain (1465 m a.s.l.), which is one of the youngest volcanoes in the Chaîne des Puys region of Massif Central in south-central France. The relative height of the peak of Puy

de Dôme from its base should be indicated. It should be also mentioned that on the top of the mountain, there is a TV transmitter antenna.

Page 14931, Section 2.2 The Air Ion Spectrometer (AIS). I recommended being a bit more specific when describing the installation of the AIS spectrometer, e.g. providing data about the place of the NAIS installation, length of sampling line, tube inner diameter and height of sampling inlet from the ground. The information about measurement cycle duration and data recording would be also very welcome.

Page 14932, lines 24-25. Radon (222Rn) measurement method (alpha spectrometry) given in Biraud et al. (2000) should be briefly introduced in this section, as the radon measurements are important part of this article. Also, installation of the device should be shortly described (e.g. measurement height from the ground, etc.), and the time-resolution of measurement data should be indicated as well.

Page 14934, lines 8-11. Regarding the assumption of negligible contribution of coarse mode aerosol particle (bigger than 420 nm) to the ion sink. Hõrrak et al. (2008) have found that this is valid for the Hyytiälä station. So, it is not generalization for all the situations and locations.

Page 14934, lines 13-15. The authors have classified the measurement days into free categories (undefined, non-event and nucleation event days) by visual inspections of the contour plots of ion size distributions measured by the AIS spectrometer. Did they use any quantitative values to discriminate between “non-event” and “event days”? If I understood correctly, all the “undefined” days have been left out from future analysis. If possible, please indicate also statistics of “undefined” and “non-event” days, e.g. in Table 1.

Page 14934, line 16. Regarding the reference to paper by Hirsikko et al. (2005). The paper by Hirsikko et al. (2005) discusses mainly the method of calculation of the size dependent growth rate of nanometer particles and statistics obtained using different instrumentation of differential mobility analyzes. The proper reference to nucleation event classification paper is Hirsikko et al. (2007b). However, the name of “bump” type event was not introduced by Hirsikko et al. (2007b), where it was classified as Ib.1 event, but later. The name “bump” type event was probably first used in the paper by Manninen et al. (2010), summarizing the earlier results. The progress in the classification of aerosol particle formation events by ion measurements can be found in Hirsikko et al. (2011). Please consider revision taking into account also other relevant papers.

Page 14936, Section 3.2 Cluster ion concentration and size. I recommend adding a table with statistical data about the concentrations of positive and negative cluster ions for different seasons and separately for event and non-event days. This table would be also helpful to get impression about the differences between the concentrations of negative and positive cluster ions discussed in Page 14936, lines 18-20. Also, it is recommended to study the annual variation (Figure 2), as well as all other time-variations of cluster ion concentrations, with respect to the factors influencing the cluster ion balance, e.g. ion sink due to aerosols, ionization rate, and ionizing radiation (caused by radon).

Page 14937, lines 18-20. It is really surprising for me that the correlation between the positive and negative cluster ions is so week in autumn, when the determination coefficient is 0.38. Could the authors give any explanation for this?

Page 14937, lines 22-23. Regarding the sentence: “It can also be seen from Table 2 that negative ion concentrations are in general higher than positive ones, with the exception of winter season.“ How do the authors explain this result in connection to the fair weather atmospheric electric electrode effect, which causes the elevated positive small ion concentration close to the negatively charged Earth ground (see Hoppel et al., 1986)?

Page 14937, lines 25-27. Regarding the sentence “This last observation supports the previous result by Laakso et al. (2007) who reported a negative overcharging of the atmosphere in Hyytiälä.” Laakso et al. (2007) studied the new particle formation

and reported the preference of negative charge on nanometer aerosol particles as an indication of ion-induced nucleation on negative cluster ions. This fact (“negative overcharging”) cannot be used directly as an indication to support the higher concentrations of negative cluster ions found in this work.

Page 14939, lines 26-29; page 14940, lines 23-26; page 14941, lines 21-22. Statements and hypotheses about the involvement of positive and negative cluster ions in the nucleation process are not well proved. The facts that positive cluster ion concentration and size distribution maximum are increasing during nucleation event days cannot be directly and solely linked to the NFP process. There can be also other processes beside the NPF, which can cause similar behavior. Also, the cluster ion size distribution maximum seems not to be the best parameter to characterize the sub 3 nm particle/ion formation and growth during the NPF events. Also the authors have stated that most of the modifications on the size distribution are observed for ions larger than 1.26 nm (Page 14942, line 12). Also, interpretation of the results of cluster ion measurements depends on the mechanism by which the cluster ions are involved into the NPF: ion-mediated or ion-induced nucleation.

Page 14940, lines 6-7 and Figure 5. Regarding the fitting procedure of log-normal distribution to measured data of negative cluster ion size distribution. How well this log-normal fitting method can be applied for the size distribution of negative cluster ions, which maximum was found to be located at considerably smaller sizes (in the range 0.9–1.1 nm) compared to positive ions, and which distribution could show considerable asymmetry? Unfortunately, there are no examples about the size distribution of negative cluster ions in the manuscript. Why not to present one example in Fig. 5?

Page 14941, lines 2-5. Regarding the sentence: “In order to compare the diameters of the cluster ion mode obtained at the Puy de Dôme with diameters from other stations, we calculated the mean value of the cluster mode diameter considering all the seasons together and we converted it into mobility.” The reader cannot understand why for the comparison of cluster ion diameters, the calculated mean diameters should be finally converted into mobilities. Please consider revision of the sentence. For the size-mobility conversions, the corresponding law should be also described. Also, the authors should keep in mind that the intrinsic parameter of ions/particles is their size, which is preferred for the comparison of the measurements carried at various locations. The mobility of cluster ions depends on mass, size and structure, as well as on air density (trough the temperature and pressure). For comparison of mobilities, the reduction to standard conditions (or some other reference values) is commonly used.

Page 14941, lines 25-29. Sorry, but I did not understand how the increase in the cluster ion diameter could result in the increase of their concentration considering the AIS measurements. If the mean diameter of cluster ion mode is increasing, the concentration of cluster ions in the fixed size (or mobility) range should diminish, because there are no cluster ions above the mobility 3.16 cm2/(V s) (corresponding to Millikan size of about 0.8 nm). The last argument is generally known fact.

Page 14945, lines 23-24. Regarding the sentence "Based on the median values in Table 4, the wet aerosol ion sink appears to be 1.07 times smaller on event days compared to non-event days,...", the authors forgot to mention that this is valid only for winter and fall, but not for entire period.

Page 14946, lines 6-7 and Table 4. The authors have mentioned that they have used both the concentrations of positive and negative cluster ions to calculate the ionization rate. Thus, the concentrations of cluster ions of both polarities are considered as factors of balance equation (Eq. 3) and, therefore, their statistics should be given in Table 4. Also, the recombination sink of positive ions should be marked as αn– instead of αn+.

Page 14946, lines 10-12. Regarding the sentence: "Based on the median values presented in Table 4, the ionization rate is higher on event days in fall, spring and especially in summer with a multiplying factor of 1.43." Looking at data in Table 4 one can see that the non-event days are showing higher median ionization rates compared

to event days, except winter. This is in contradiction with the sentence above. The ionization rates are equal in fall (autumn), and they are probably nearly equal also in spring, considering measurement uncertainties. Only summer shows a considerable difference.

Page 14948, Section 3.3.3 Estimation of the ionization rate based on radon measurements. In this section I would expect to see some statistical data of radon activity-concentration measurements at Puy de Dôme, as well as short discussion about radon concentration variation.

Page 14948, lines 24-28. Laakso et al. (2004) showed that during early spring, when the ground was covered by snow, the external radiation (gamma and cosmic rays) was the main ionization source, but it was more stable compared to radon, which caused the most of variation in the ionization rate. However, also the external radiation showed smooth trends. So, considering annual periods, the variation caused by gamma radiation cannot be ignored. The latter was clearly shown by Hirsikko et al. (2007a). Therefore, the Section 3.3.3 should be revised taking into account the real estimates of gamma radiation measurements at Puy de Dôme.

Page 14949, lines 2-4 and Figure 12. The authors should explain what they mean about "the measured and the calculated ionization rates are on average in good agreement". The data-points in Figure 12 are quite scattered and it is difficult to find out relationship between the physical parameters.

Page 14949, lines 10-11. Regarding the statement about invalidity of the steady state balance equation. The disbalance due to non steady-state situation can take place only during sudden changes in the ionization rate or in the cluster ion sink due to aerosols. These changes should be faster or comparable with the characteristic lifetime of cluster ions (in the clean atmosphere about 5 min). The balance of small ions in the atmospheric air can be attained typically during 5-10 min considering different ion sink rates caused by aerosol particles, see e.g. Israel et al. (1970). So, I do not think that this (non-steady-state situation) can be a reason of uncertainties as there are probably not any pollution sources in the vicinity of station. This comment concerns also conclusions in Page 14950, lines 11-18 and Page 14952, lines 6-9.

Page 14949, lines 20-22. Regarding the gamma radiation contribution to the ionization rate. The choice of the constant value of 1.7 ion pair per ccm an second, based on the work by Laakso et al. (2004) carried out at Hyytiälä station, cannot be accepted. See comment above.

Page 14949, lines 25-27. Regarding the sentence: "This observation indicates that when estimating the ionization rate from direct measurements we are missing a source, which is linked to a temperature dependant process." This result is totally different from that of other recent works in this field, e.g. Laakso et al. (2004), Tammet (2006), Hõrrak et al. (2008), Schobesberger et al. (2009), which have been looking for missing additional sink of cluster ions instead of extra source, when comparing the ionization rates calculated from the balance equation of cluster ions and estimated from the ionizing radiation measurements. Probably, this result will be revaluated when the real measurements of gamma-radiation at Puy de Dôme are taken into account.

Page 14952, line 6-11. I agree, that there could be an imbalance between cluster ion sources and sinks. However, the statement that this imbalance is due to non-steady-state conditions is not proven enough to declare it in conclusions, considering the other possible uncertainties. Please consider revision of the text.

Technical corrections:

Page 14927, manuscript title. I would leave out the word "positive", as the negative cluster ions are also discussed in the paper. Alternative is adding the word "negative".

Page 14929, line 18. The acronym of the NAIS spectrometer should be decoded as the Nanometer aerosol and Air Ion Spectrometer.

Page 14932, line 26. The abbreviation LWC (liquid water content) should be explained.

Page 14938, lines 3-8 and Figure 3. Regarding the diurnal variation of cluster ion concentration. It would be good if the authors will find possibility to increase the vertical size of the sub figures in Figure 3 to make the changes in hourly medians more clearly visible. The same can be mentioned about the Figure 6 in page 14968.

Page 14941, lines 6-16. Regarding the accuracy of the parameters (decimal places of the numbers). Please consider the measurement uncertainties to found out appropriate number of decimal places.

Page 14950, line 20. Instead of "mobility diameter", there should be "mobility".

Page 14951, lines 10-11. Regarding the fragment "The mode diameter of the positive cluster ion mode". The first "mode" could be deleted.

Page 14951, line 20. The fragment "the wet SMPS size distribution" sounds strange, consider revision.

Page 14951, line 21. Please correct the numbers "2.310-3–10.210-3".

Page 14953, Equation A2 in line 3. Please check its correctness, taking into account the Equation 4, which contains an integral over the size distribution of particles.

Page 14959, Table 1. If not troublesome, please add an extra line with the total number of events and corresponding statistics. Also, the data about measurement period and location will be very welcome.

Page 14960, Table 2. The same comments as for Table 1. Please add extra line with the data for the entire measurement period.

Page 14966, Figure 4. What do the colors (from blue to brown) mean in the Figure 4?

Page 14961, Table 3. An explanation for the correlation coefficient R should be given.

Page 14974, Figure 12. Meaning of four figures is not explained in the figure caption. One can expect reading the manuscript text that they correspond to four seasons.

Typing errors:

Page 14930, lines 2 and 4. Instead of “Milikan” should be Millikan, as reference to Robert Andrews Millikan. See also page 14931, line 22.

Page 14936, line 9. Instead “no NPF” should be “non-NPF”

Page 14938, line 1. Instead of ”Thakuse”, there should probably be “Tahkuse”.

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