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.

C. Rose et al.

c.rose@opgc.univ-bpclermont.fr

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We thank Referee N°2 for his numerous comments and remarks which greatly helped us to improve the manuscript. We agreed with most of the suggestions and have done our best to follow them. Our answers are reported below.

Specific comments:

Comment 1: 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

C6867

(1994), Tammet et al. (2006), (Hirsikko et al., 2007b) 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).

Reply 1: All the proposed papers were added to the introduction and/or to the discussion part.

Comment 2: 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.

Reply 2: At the Puy de Dôme, it is very clear that positive cluster ions show higher concentrations and diameter on event days compared to non-event days while it is not so clear for negative ones. This observation may need to be mentioned as contrary to some other studies. Thus the reported sentence was changed to: "Contrarily to observations reported from some previous studies (Wilhelm et al., 2004;Laakso et al., 2007;Enghoff and Svensmark, 2008), at the Puy de Dôme, positive cluster ions exhibited more variation in their properties (concentration and size) between event and non-event days compared to negative ones".

Comment 3: 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,

C6868

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.

Reply 3: It is true that a table can ease the general understanding of the results and is a good way to summarize the comparison between the two polarities. Thus, a table, referred as Table 3, was added to Section 3.2, as suggested. However, only measurements from clear sky conditions are reported, since cloudy conditions are beyond the scope of this study . Moreover, the influence of clouds on small particles at the Puy de Dôme was already discussed in the paper byVenzac et al. (2007).

Comment 4: 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.

Reply 4: We decided to consider positive as well as negative ions in the first part of this study which gives an overview of the concentrations from long term measurements. When comparing event and non-event days, the behavior of positive cluster ions appeared more remarkable than the one of negative ions, this is the reason why only the positive clusters were further discussed. Concerning the first part of the study mentioned above, we felt that showing all the figures for the two polarities would weigh the paper which already contained 13 figures. Since positive ions were the thread of our study, we decided to show only the figures concerning the positive polarity and comment in the next the behavior of negative ions. In the literature we found several examples of studies discussing the two polarities in the text but showing only the figure for one of the polarities (e.g. Hõrrak et al., 2003; Boulon et al., 2010).

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

Reply 5: We refer to mobility diameter, i.e. Millikan diameter when converting the measured mobility to the particle diameter. The corresponding reference, Mäkelä et al., 1996, is now mentioned in the introduction as well as in Section 2.2.

Comment 6: Page 14931, Section 2.1 Measurement site. The Puy de Dome 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.

Reply 6: A more detailed description of the measurement site is now proposed: "Measurements were conducted at the Puy de Dôme (PDD) site in central France (45°46' N, 2°57' E) which is part of networks EMEP/GAW/ACTRIS. The station is located at the top of the Puy de Dôme mountain (1465 m a.s.l) which is one of the youngest volcanoes of the Chaine des Puys. It is also the highest, with a height of 550 m relative to its base. The station is situated in an environment mainly characterized by fields and forest but one should note the presence of a TV transmitter antenna (73 m high) closed to the station, at the top of the mountain. The nearest city, Clermont-Ferrand (300 000 inhabitants), is located 16 km East of the mountain."

Comment 7: 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.

Reply 7: More information was provided concerning the instrumental setup used during the measurement period in the general description proposed at the beginning of

Section 2.2: "During the whole measurement period, three different instruments were used, being AIS 7, NAIS 3 and NAIS 13. From February 2007 to the end of 2010, the instrument was operating in a shelter, with a short inlet (length 30cm, inner diameter 3 cm) sampling approximately 2 m high from the ground. At the end of 2010, the instrument moved on the roof of a new station located closed to the temporary shelter, sampling 11m high from the ground with the same individual non-heated short inlet. For the two different measurement setups, one should note that measured ion size distributions were directly influenced by the presence of a cloud". More information concerning the measurement cycle was also provided: "During the whole measurement period and for the three instruments, the offset cycle was at least as long as the measurement cycle to ensure the a good signal to noise ratio".

Comment 8: 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.

Reply 8: It is true that an important part of this study deals with radon measurements. Thus, more information on the measurement technique was provided in a new section "2.3 Radon Measurements". The setup is described as follow: "Radon at Puy de Dôme is measured with the active deposit method (Polian et al., 1986; Biraud et al., 2000). The method is based on the measurement of 222Rn daugters (218Po, 214Bi, 214Po) which are absorbed onto atmospheric particles. Total active deposits of those daughters are accumulated on a cellulose filter during one hour (air is sampled on the roof of the station, 11m above the ground). Then the filter is automatically moved under one alpha detector coupled to a photo-multiplicator. Total α radioactive decay is measured every 10min during one hour. The measurement error is estimated to be 10 to 20% (Polian et al., 1986). A correction is performed on the calculated 222Rn activities to consider the radioactive disequilibrium between 222Rn and its short-lived daughters.

A disequilibrium factor of 1.15, like the one estimated by Schmidt, (1999) for a similar mountain station at Shauinsland, was used for correcting the data".

Comment 9: 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.

Reply 9: In order to evaluate the influence of coarse particles on the ion sink, we calculated the ion sink from OPC GRIMM size distributions (0.35-17.5μm) obtained between February 2010 and December 2011. When calculating the ratio of the sink derived from the OPC to the sink derive from the SMPS, we obtain a median ratio of 0.0123 (25th percentile: 0.0069; 75th percentile: 0.0214) if we use dry diameters and a median ratio of 0.0208 (25th percentile: 0.0110; 75th percentile: 0.0384) if we use wet diameters. Thus, it appears that the contribution of coarse particles to the ion sink is negligible at the Puy de Dôme. This information was added to the text in Section 2.5.1.

Comment 10: 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.

Reply 10 : The classification of the measurement days has been done exclusively by visual inspections of the contour plots of ion size distribution according to the method suggested by Dal Maso et al. (2005) (this reference was added in Section 2.4.2). We know that some methods for the automatic detection of regional new particle formation events have been recently developed Kulmala et al. (2012), certainly leading to less

subjectivity in the classification, but we used the original method for two main reasons. First, this method has been commonly used until now(e.g.Boulon et al., 2010; Manninen et al., 2010) and it is still the starting point for more detailed classifications (e.g. Yli-Juuti et al., 2009; Vakkari et al., 2011). Moreover, this is the method used in the study by Boulon et al. (2011) on which is based the classification of the days for the time period February 2007 – June 2010. In order to be consistent with this previous work, the classification from July 2010 to February 2012 was done in the same way. Undefined days were not analyzed in this study since we only found 10 of them. The statistics concerning undefined as well as non-event days were added to Table 1.

Comment 11: 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. (2007a). However, the name of "bump" type event was not introduced by Hirsikko et al. (2007a), 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.

Reply 11: We clearly made confusion by mentioning(Hirsikko et al., 2005). We changed this reference to the more appropriate one (Hirsikko et al., 2007a) and we also added some relevant papers to highlight the classification that we used. It is true that bump type events were not present in the classification by (Hirsikko et al., 2007a) .They were introduced by Vana et al. (2008) but they were called "hump" instead of "bump". Both are used (e.g. Yli-Juuti et al., 2009; Manninen et al., 2010) but we keep "bump" in our paper, again to be consistent with the work by Boulon et al. (2011).

Comment 12: Page 14936, Section 3.2 Cluster ion concentration and size. I rec-

ommend 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).

Reply 12: As previously mentioned in Reply 3, a Table was added to Section 3.2 to ease the comparison between the two polarities. Section 3.2 includes analysis of the annual as well as the diurnal variation of different ion properties (concentration, size) for the different seasons and studies the variations of these properties regarding the occurrence of a new particle formation event. We do believe that the study of variations of concentrations as a function of separate parameters (e.g. ion sink, ionization rate, ionization radiation) is very confusing, as the concentrations depend on both sources and sinks at the same time. Hence we chose to directly discuss the variation of concentration as a function of the difference between sources and sinks in the balance equation.

Comment 13: 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?

Reply 13: Data was checked to filter out bad measurement periods caused by instrument failures, which thus cannot explain the weak correlation in autumn. However, we have no robust explanation for this observation.

Comment 14: 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))?

Reply 14: The reported sentence obviously needs to be rephrased with more caution, since the concentrations from the two polarities do not show huge differences. It would certainly be more accurate to say "It can also be seen from Table 2 and Table 3 that negative ion concentrations are in general slightly higher than positive ones, with the exception of winter season which displays very similar concentrations for the two polarities". However, it is true and worth to mention that, except in winter, our observations contrast with what would be expected with the electrode effect. Thus, a more complete discussion on the observed concentrations was included in Section 3.2: "At the Junfraujoch station, lower negative cluster ion concentrations were also reported by Vana et al. (2006). According to the authors, lower pressure conditions at high altitude increased the mobility of cluster ions, which could eventually exclude the smallest clusters (especially negative) from the measurement range of the instrument. The fact that at the Puy de Dôme negative ions are, with the exception of winter, slightly more numerous than positive ones, contrasts with what would be expected from the atmospheric electrode effect. Indeed, this effect predicts that in fair weather, higher positive cluster ion concentrations should be detected near the ground and up to a few meters because of the negative charging of the Earth (Hoppel et al., 1986). At the Puy de Dôme, horizontal and vertical winds from the valley are often observed. This turbulence mixes the air, which may hide or suppress the effect of electric field, and thus partly explain why positive ions are not found to be predominant".

Comment 15: 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.

Reply 15: The connection between the negative ion concentration and the negative overcharging of the atmosphere was obviously not very appropriate. Thus, the litigious sentence was removed and a more complete discussion on the positive and negative concentrations was proposed, as suggested by Comment 14.

Comment 16: 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.

Reply 16: It is true that cluster ion properties can be influenced by other processes than NPF. Thus a more conditional formulation was adopted for the reported sentences from page 14939 and 14941. However, on page 14940, we do believe that the sentence is fair enough with the use of the word "potentially". Page 14939: "The dissimilarity in the different diurnal variations between the two polarities at the Puy de Dôme, especially in summer and fall on event days, however indicates that positive and negative cluster ions could be concerned by nucleation, but with unequal involvements in the process". Page 14941: "Particularly, positive cluster ions exhibited more variation in their properties (concentration and size) between event and non-event days compared to negative ones. This observation suggests that positive cluster ion characteristics might be more

significantly impacted by the occurrence of a NPF event than negative ones".

Comment 17: 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?

Reply 17: The log-normal can be applied to measured negative cluster ion size distributions since the maximum concentration of the cluster ion mode is clearly visible. As suggested and in order to highlight this statement, an example of a negative cluster ion size distribution was added to Fig. 5.

Comment 18: 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.

Reply 18: The purpose of the analysis reported on page 14941 was to compare the diameter of the cluster mode observed at the Puy de Dôme with the diameter of the

cluster mode reported for other stations. Since most of the references in literature reports mobilities, we finally converted cluster mode diameters from the Puy de Dôme into mobilities. However, it is obviously not so straightforward to compare mobilities, which especially depend on temperature and pressure. Thus, only the comparison with the results from Manninen et al. (2009), who provided diameters, was retained for the discussion.

Comment 19: 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.

Reply 19: We do not agree with the fact that there is no cluster ions above the mobility 3.16 cm2/(V.s), which is only the upper detection limit of the AIS. The fact that the size of the ions in the cluster mode could impact the concentration measured with an AIS was already proposed by Vana et al. (2006). Indeed, they measured smaller negative cluster ion concentrations compared to positive ones at Jungfraujoch (3500 m a.s.l). They explained this observation by the fact that high altitude, and thus lower pressure, lead to higher ion mobilities, which finally excluded the smallest ions (especially the negative) from the measured range of the instrument.

Comment 20: 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.

Reply 20: After the corrections made according to Comment and Reply 21 detailed right after, the sentence was completely changed to: "Based on the median values

in Table 5, the wet aerosol ion sink appears to be similar on event and non-event days during the cold season whereas during the warm season the sink is on average increased by a factor of 1.25 on event days compared to non-event days."

Comment 21: 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 $\alpha n-$ instead of $\alpha n+$.

Reply 21: We thank the referee for pointing out the bad notation, which in fact lead us to find mistakes in the statistics reported in Table 4 (now Table 5). Indeed, some of the values had been calculated without filtering RH>90% properly. We finally recalculated all the values, which did not change any of our conclusions but only some numerical values. We also added some information on the cluster concentrations which are of course factors of the balance equation. The effect of fog and moisture on small ion concentrations was mentioned when comparing small ion concentration from Table 4 and newly added Table 3.

Comment 22: 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.

Reply 22: Exact, values are similar on event and non-event days in winter, spring and fall and they are higher on non-event days in summer, even with the corrections made

according to Reply 21 from the Specific comments. The sentence was changed to: "Based on the median values presented in Table 5, the ionization rate displays similar values on event and non-event days for all the seasons except summer, which is characterized by median ionization rates 1.18 times higher on non-event days compared to event days".

Comment 23: 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.

Reply 23: Some statistics concerning radon activity concentration as well as a short discussion on the variation of the radon concentration are now included in the text, at the beginning of Section 3.3.3.

Comment 24 : 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. (2007b). Therefore, the Section 3.3.3 should be revised taking into account the real estimates of gamma radiation measurements at Puy de Dôme.

Reply 24: This is a good comment. Considering studies by Hirsikko et al. (2007b) or Franchin (2009), it is clear that the external radiation contribution to the ionization rate exhibits a seasonal variation with higher values in summer and fall. Thus, even if the seasonal variation does not impact daily scale variations that can be seen between event and non-event days and which are of interest in this paper, more accurate estimations of the gamma dose rate were considered. Since no appropriate external radiation dose rate measurements were available for the Puy de Dôme (Billon et al.

(2005) only gives orders of magnitude with no seasonal indication), we finally used values from a more similar site than Hyytiälä: i.e. at BEO Moussala, Bulgaria, which is a high altitude station (2925 m a.s.l.). In Section 3.3.3, the main focus is maintained on the quickly varying component of ion production, radon, since the main purpose of the analysis is to find the link between ion production and increased ion concentration on event days. In order to discuss the contribution of external radiation (which does not show daily cycle) on ionization rate and to give more relevant numerical values of the measured ionization rate, an additional Section 3.3.4 is now proposed. When using measurements from BEO Moussala, the contribution to the ionization rate from external radiation that we finally obtain are 10.09, 9.74, 11.76 and 11.14 cm-3s-1, from winter, spring, summer and fall, respectively. These values are similar to the median value reported by Franchin (2009)for Hyytiälä (10.12 cm-3s-1) and significantly exceed ionization rates derived from radon measurements (0.94-1.57 cm-3s-1). However, the variability of the calculated ion source is very similar to the variability of the ionization rate derived from radon, indicating that external radiation contribution to the ion source is at a stable level that do not influence the ion concentration variability observed at Puy de Dôme.

Comment 25: 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.

Reply 25: Our answer to this comment will be similar to the one provided for Comment 4 from Reviewer 1. When considering all the seasons together, with both event and non-event days, we obtain the difference between calculated and measured ionization rates in the range 0.19±2.26 cm-3s-1, which indicates that ionization rates obtained from the two different methods are on average not so different. However, we must recognize that for some couples of values the differences are not negligible, and in that case imbalance between sources and sinks seem to be a plausible explanation. Thus,

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we finally replaced the sentence "For all seasons, the measured and the calculated ionization rates are on average in good agreement" by "On average, the measured and the calculated ionization rates are of the same order of magnitude and display the same temporal variations at the intra seasonal scale".

Comment 26: 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. Israël (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.

Reply 26: We do not fully agree with the Reviewer. Indeed, we do think that, if there is a constant additional source on event days during the nucleation process, it can affects ion concentrations on time periods longer than 5min, and thus cause non steady state conditions. Moreover, this hypothesis was fully accepted and used by Reviewer 1 to explain discrepancies between measured and calculated ionization rates.

Comment 27: 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.

Reply 27 : A more complete discussion about the influence of the variation of the external radiation contribution was added to the text in a new section (3.3.4) as suggested by Comment 24.

Comment 28: Page 14949, lines 25-27. Regarding the sentence: "This observation

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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.

Reply 28: When taking into account more accurate seasonal values for the external radiation, we still observe a correlation between the temperature and the difference between measured and calculated ionization rates. However, this correlation could only be due to the use of a mean contribution of the external radiation over a given season, and could not be connected to an additional source linked to a temperature dependent process. Hence, the discussion concerning this correlation was removed from the text, as well as Fig. 13.

Comment 29: 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.

Reply 29: According to Comment 26, discussions, and especially conclusion, were revised. The final sentences of the conclusion are now: "Further analysis will be required to eventually identify an additional source that could explain the higher positive cluster ion concentrations at the beginning of the NPF process. Such an extra source would cause an imbalance between sources and sinks, avoiding an appropriate use of the balance equation on event days".

Technical corrections

Comment 1: Page 14927, manuscript title. I would leave out the word "positive", as the negativecluster ions are also discussed in the paper. Alternative is adding the word "negative".

Reply 1: The word Âń positive Âż was finally left.

Comment 2: Page 14929, line 18. The acronym of the NAIS spectrometer should be decoded as the Nanometer aerosol and Air Ion Spectrometer.

Reply 2: The signification of the acronym may have changed but according to the recent paper by Mirme and Mirme (2013), it seems that NAIS currently stands for "Neutral cluster and Air Ion Spectrometer".

Comment 3: Page 14932, line 26. The abbreviation LWC (liquid water content) should be explained.

Reply 3: The signification of the abbreviation is now given in the text.

Comment 4: 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.

Reply 4: It is true that Fig. 3 and 6 are not very easy to read but we did not find any apropriate solution to improve the quality of the figure without removing information (10th, 25th, 75th and 90th percentile) or multiplying the number of different figures, which is already high in the paper.

Comment 5: 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.

Reply 5: The concerned numerical values were removed as mentioned in Reply 18 from Specific comments.

Comment 6: Page 14950, line 20. Instead of "mobility diameter", there should be "mobility".

Reply 6: That's true. The word "diameter" was removed.

Comment 7: Page 14951, lines 10-11. Regarding the fragment "The mode diameter of the positive cluster ion mode". The first "mode" could be deleted.

Reply 7: The first "mode" was suppressed.

Comment 8: Page 14951, line 20. The fragment "the wet SMPS size distribution" sounds strange, consider revision.

Reply 8: "The wet SMPS size distribution" was replaced by "The SMPS size distribution, considering wet aerosol particle diameters".

Comment 9: Page 14951, line 21. Please correct the numbers "2.310-3–10.210-3".

Reply 9: The sign for the multiplication was added.

Comment 10: 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.

Reply 10: It is true that Equation A2 was not written in a proper way considering the integral in Equation 4. Correction was made.

Comment 11: 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.

Reply 11: An extra line was added to Table 1 with information on the entire measurement period. Also, information on the location and the measurement period was added to all figure captions and table headings.

Comment 12: Page 14960, Table 2. The same comments as for Table 1. Please add

C6885

extra line with the data for the entire measurement period.

Reply 12: An extra line was added for the whole measurement period and the heading contains more information.

Comment 13: Page 14966, Figure 4. What do the colors (from blue to brown) mean in the Figure 4?

Reply 13: The colors used in Fig. 4 as well as in Fig. 7 have no special signification, except that the change in colors follows the time evolution.

Comment 14: Page 14961, Table 3. An explanation for the correlation coefficient R should be given.

Reply 14: An explanation was added in the table heading: " is the correlation coefficient between the obtained from measurements and the corresponding parameterized values".

Comment 15: 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.

Reply 15: We clearly forgot to specify the meaning of the four figures, which correspond to the four seasons. Information was added. Typing errors

All suggested corrections were made.

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