Reply to Referee #1

We thank Anonymous Referee #1 for their helpful and constructive comments. We have answered to the comments below. Bold text is quoted from the referee's comments, and the text in italics has been added to the manuscript.

GENERAL COMMENTS:

Contribution of ions in new particle formation has long been a topic of research and scientific debate. In earlier studies (e.g. Kulmala et al., 2013) neutral cluster production via ion-ion recombination has been described by simplified balance equation which takes into account ion-ion recombination and loss via coagulation. This work has completed the simplified balance equation by taking into account additional plausible processes, like growth of recombined clusters. In the manuscript, effect of cluster growth on neutral cluster concentration estimation was analyzed. This work fits well in the line of works which either experimentally or theoretically have tried to investigate neutral cluster formation via ion-ion recombination. This work can be published with minor corrections. In addition to comments by the other referee, following suggestions to further improve the manuscript should be considered.

SPECIFIC COMMENTS

Abstract, page 20810, lines 2-5: At this point of the manuscript it is not clear to reader what is new in methods used here. One or two sentences of what was done and what is new should be added. Conclusions, page 20822, lines 25-26 should be revised accordingly.

We added the following sentences to the abstract (page 20810, line 5 in the ACPD version):

Our method takes into account the production of recombination products in the collisions between oppositely charged ions and the loss due to coagulation. Furthermore, unlike previous studies, we also consider the effect of condensational growth on the size distribution of recombination products.

In addition, we modified the first paragraph of the conclusions, which now includes the following sentences (page 20822, line 27 in the ACPD version):

This method takes into account the production of recombination products in the collisions between oppositely charged ions and the loss of them by coagulation. In addition, contrary to earlier studies, the loss and gain of recombination products due to condensational growth are also considered.

Abstract, page 20810, lines 12-15: The observed small fraction of ion-ion recombination products from total neutral cluster concentration is consistent with earlier studies. However, I think that the authors should emphasize in the abstract and conclusions that taking into account growth of clusters has large influence on results (page 20822, lines 4-24). When cluster growth is included in the analysis the authors could estimate maximum production of

neutral clusters from ion-ion recombination by deploying λ (maximum fraction of stable recombination products) equal to 1. If growth is not taken into account λ gets experimental values between 0.1 and 1 in order to provide reasonable estimates for recombination product concentrations. I think this is one of the most important results of this work but it is only shortly mentioned in the conclusions and not at all in the abstract.

We modified the abstract to emphasize the effect of condensational growth on the results. It now includes the following sentences (page 20810, line 12 in the ACPD version):

We also investigated how the results change if the effect of condensational growth is neglected. It seems that with that assumption the fragmentation of newly-formed recombination products has to be taken into account, or else the concentration of recombination products is overestimated.

This issue is now clarified also in the conclusions, which now includes the following sentences (page 20824, line 4 in the ACPD version):

We also examined how the fraction of recombination products of all neutral clusters changes if the effect of condensational growth is assumed to be negligible. It seems that in this case we cannot anymore neglect the fragmentation of newly-formed recombination products because by doing so we end up overestimating the concentration of recombination products. Therefore, we used the method presented by Kulmala et al. (2013) to estimate the maximum fraction of stable recombination products. By using this method we obtained lower values for the fraction of recombination products of all neutral clusters than when the effect of condensational growth was taken into account.

Page 20811, line 30-page 20812, line 1: Methods to estimate growth rate and coagulation sink are from earlier studies. This sentence needs to be revised accordingly.

In earlier studies it has not been properly explained how the production rate of recombination products is calculated, and the gain and loss of recombination products due to condensational growth have not been considered. Therefore, we do not think that it is necessary to revise the sentence.

Page 20816, line 9-11: There are some inaccurate descriptions in the manuscript. As an example, the growth rate method needs to be explained a bit more clearly here since results depend strongly on growth rate. On page 20821, before discussing the last figure, first explanation of done growth rate analysis is finally given. Additionally, explain here why this method was chosen.

We modified the sentences explaining the growth rate methods in the section 2.2.2 to make them clearer. Now the sentences read (page 20816, line 9 in the ACPD version):

The estimates for growth rates (GR_i), needed for the condensational growth term, we can obtain from cluster diameter vs time data presented by Kulmala et al. (2013). The values for growth rates in each size class can be obtained by fitting the data with a 3rd degree polynomial, and differentiating (Table 1).

In the analysis explained on the page 20821, the lower growth rates are assumed to examine the sensitivity of the results to growth rates. This is done as we do not know if the used growth rates are representative regarding the whole measurement period. This is already explained in the manuscript as follows (page 20821, line 11):

However, in reality, these growth rates may not be representative regarding the whole measurement period, which also includes time periods with no new particle formation. Thus, in this section we aim to assess how sensitive the obtained results are to uncertainties in the growth rates.

Page 20818, first paragraph: This paragraph is difficult to follow and should be revised. The λ is one of the important variables which have large influence on results. Readers should not first have to go through other references before generally understanding what was done in this work.

As the method to determine λ is properly explained in the supplementary material of Kulmala et al. (2013), we think that it is unnecessary repetition to explain the procedure in more detail here.

Page 20820 and 20835, Fig 4: Add error bars based on concentration measurement and mobility/size interval uncertainties which can be large. There should be discussion in the text what is different in Fig. 4 and corresponding figure in Kulmala et al. (2013). I think that this is good point to clarify reason for different temporal evolution of total neutral cluster and recombination product concentrations. Similarly, short analysis based on Fig 5 should be given.

The error estimate for the total neutral cluster concentration due to measurement uncertainties is 100–200 cm^{-3} as already mentioned in the section 2.1. However, estimating the error of the recombination product concentration is practically impossible, as such many assumptions are made when deriving the equation for the recombination product concentration. For that reason we do not think that adding error bars in Fig 4 is necessary.

Still, we added more discussion about the temporal variation of the concentrations as the referee suggests. Now the second to last paragraph in the section 3.1 reads (page 20820, line 8 in the ACPD version):

From Fig. 3 it can also be noticed that the fraction of recombination products of all neutral clusters had a strong temporal variation during the measurement period, making the ranges from 25th to 75th percentiles wide. The strong variation in the concentration of recombination products and their contribution to cluster concentrations can also been seen in Fig. 4, where the time series for the concentrations of recombination products and all neutral clusters between 0.9 and 2.1 nm are presented. In addition, Fig. 4 shows that the recombination product concentration did not have a similar diurnal cycle as the total neutral cluster concentration which increased strongly during daytime. The reason for the difference is that the concentration of recombination products depends mainly on relatively stable ion concentrations whereas the total neutral cluster concentration increases when there is new particle formation taking place. This can be seen in Fig. 5 as well, where the median diurnal variations of the concentrations of recombination products and all

neutral clusters are depicted for new particle formation event and non-event days. Figure 5 also shows that the concentration of recombination products was on average slightly higher on new particle formation event days than on non-event days, except for the afternoon hours.

Page 20824: What is authors' recommendation which method should be used in other studies in future: the presented method with growth rates from new particle formation event periods or the simplified method used in earlier studies?

In our opinion, the effect of condensational growth should be considered if the growth rates are known. To state this more clearly in the manuscript, we modified the last paragraph of the conclusions. The beginning of the paragraph now reads (page 20824, line 11 in the ACPD version):

Overall, our method can be assumed to provide a reasonable maximum estimate of the contribution of recombination products to atmospheric cluster concentrations. In the light of our results, it seems that the effect of condensational growth on the size distribution of recombination products should not be neglected, provided that the values for the cluster growth rates are known.

Figures 1-3 and 6: Are data from whole measurement period considered in these figures?

Yes, in all figures except for Fig. 4 and Fig. 5 the data from the whole measurement are presented.

TECHNICAL COMMENTS

Page 20811, line 20: Work by Tammet et al. should be cited in the introduction.

Reference to the paper by Tammet et al. was added (page 20827, line 14 in the ACPD version):

Tammet, H., Hõrrak, U., Laakso, L., and Kulmala, M.: Factors of air ion balance in a coniferous forest according to measurements in Hyytiälä, Finland, Atmos. Chem. Phys., 6, 3377–3390, 2006.

Page 20828: remove reference from table caption.

The reference was removed.

Page 20831, table 4: round values are accurate enough for concentrations Nx.

We replaced too accurate values with rounded ones.

Page 20832: Is error bar appropriate name for 5th and 95th percentiles?

To be more precise, we replaced "error bars" with "vertical bars" in all figure captions.