Reply to Referee #2

We thank Anonymous Referee #2 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

This study investigates the role of ion-ion recombination on the formation of sub-2nm articles by comparing the calculated concentration of the recombination products with the measured concentration of total sub 2nm clusters. Authors conclude that the contribution is highest at 1.5-1.9 nm diameter range, and their results shows that ~10% of the total electrically neutral particles is produced by the recombination within 1.5-1.9 nm diameter range. The authors analysis clearly shows that the neglecting the particle growth overestimates the concentration of recombination products. The authors describe a new method for obtaining the collision pair among oppositely charged ions from different mass classes. I believe that this study satisfies the requirements on the scientific quality of the ACP journal; therefore, this paper deserves to be published in ACP. However, authors need to add some discussions on the assumptions they made in their analysis. In addition, the value of this paper would greatly increase if authors can explain the reasons for the vastly different conclusions made by this study and some previous theoretical studies which claim that ion-mediated nucleation can have significant contribution to the new particle formation.

More discussion about the assumptions made in our analysis was added according to the comments of the referee. We also modified the last paragraph in the section 3.1 to discuss more the disagreement between the experimental studies and some model simulations. Now the paragraph reads (page 20820, line 22 in the ACPD version):

The obtained results are in reasonable agreement with the results of earlier studies, in which the concentration of recombination products has been calculated from Eq. (6) not including the condensational growth term. Recently, Kulmala et al. (2013) concluded that on average only a minor fraction of sub-2 nm neutral clusters observed in Hyytiälä originate from ion–ion recombination. By measuring the concentrations of sub-3 nm particles at the same site, Lehtipalo et al. (2009) observed that the fraction of recombination products of all neutral clusters is on average low (~5%) but varies a lot from day to day. Furthermore, the comparison between the formation rates of neutral clusters due to ion–ion recombination and the total particle formation rates indicates that ion-ion recombination has only minor contribution to particle formation in boreal forest (Kulmala et al., 2007; Manninen et al., 2009a). However, the model simulations by Yu and Turco (2008) suggest much greater significance for recombination than the studies based on field measurements. This discrepancy illustrates the fact that the details of the dynamics of sub-3nm charged and neutral clusters are still not well known. This makes both the modeling and the theoretical calculations of ion-ion recombination process challenging. In addition, the uncertainties in measuring the size distributions of neutral and charged clusters in this size range are also relatively large. For more discussion about the role of ion-mediated processes in atmospheric new particle formation, see Hirsikko et al. (2011).

TECHNICAL COMMENTS

1. Authors assume the same relationship between the electrical mobility and mass for both positive and negative ions. Chemical identities of atmospheric positive and negative ions are different. For example, Figure 2 of (Swider 1988) shows the different trend between positive and negative small ions. Mass-mobility relation for tropospheric positive ions are also given by (Dolezalek et al. 1977). Authors should discuss how the proposed approach needs to be modified if the mass-mobility relation is polarity dependent.

If it was taken into account that the mass-mobility relation depends on the polarity, the conversion of the mobility bins measured with NAIS to mass bins should be done separately for negative and positive ions. The different mass ranges of negative and positive ions would then be used to calculate the mass ranges of recombination products formed in different collisions. To make it clear that in reality the mass-mobility relation may depend on the polarity, the following sentence was added to the section 2.2.2 (page 20817, line 3 in the ACPD version):

In addition, the relationship between ion mobility and mass may in reality depend on the polarity (Swider, 1988).

2. Authors assumes the same recombination rate (1.6*10ˆ-6 cmˆ3/s) for all collision pairs. (Natanson 1959) shows the theoretical expression for the recombination coefficient between two ions having different mass. The expression can also be found and explained well in (Gringel et al. 1978). Authors should discuss how the results would change if the mass of the collision pair, which affects the relative velocity of colliding ions, was included in the calculation of the recombination rates.

We thank the referee for the good comment. It is, indeed, true that recombination coefficient may in reality depend on the masses of colliding ions. However, estimating how this effect would affect recombination coefficient and thus change our results is not straightforward but actually a difficult theoretical problem. Furthermore, to be accurate, we should also consider how environmental conditions, especially temperature, affect recombination coefficient. However, this is also not a simple task (for discussion about recombination coefficient in different conditions, see e.g. Bates et al. 1985). Thus, we think that the analysis of the variation of recombination coefficient is beyond the scope of our study. However, to emphasize that, in reality, recombination coefficient may not be constant, we added the following sentence to the section 2.2.1 (page 20813, line 9 in the ACPD version):

However, it has to be noted that, in reality, these coefficients may not be constant but depend on the properties of colliding ions or particles and environmental conditions (Bates, 1985; Hoppel and Frick, 1986).

In addition, we modified the last paragraph of the conclusions to make it clear that recombination coefficient may depend on the masses of colliding ions. Now the paragraph includes the following sentence (page 20824, line 15 in the ACPD version):

In addition, the dependency of the recombination coefficient on environmental conditions, especially on temperature, and on the masses of colliding ions should be understood better, so that it could be included in the calculations.

3. Authors should add some discussion on the effect of the size-mobility relation on the calculated concentration of recombination products since the scavenging rate is sensitive to the particle size of the recombination products. It is not clear why authors chose not to use the more recent size-mobility relation such as Equation 1 in (Ehn et al. 2011). Since authors also have information on the ion mass the expression given in (Ehn et al. 2011) should give better estimate of the true particle diameter. (Tammet 1995; Okada et al. 2011) also discuss that for a given value of mobility the size of an electrically neutral particle is larger than the size of an electrically charged particle since the polarization effect reduces the mobility of the charged particle.

As the referee points out, the equation presented by Ehn et al. (2011) for the size-mobility conversion should be more accurate than Eq. (8) used in the manuscript. Consequently, we decided to replace Eq. (8) with the equation presented by Ehn et al. (2011) in our analysis. The text was modified accordingly (page 20817, line 11 in the ACPD version):

Thereafter, we may convert the mobilities into mobility diameters using the modified Stokes-Millikan equation, which takes into account the finite mass of the particle (Tammet et al., 1995; Ehn et al., 2011):

$$d_p = \frac{1}{\sqrt{1+\mathrm{m_g}/\mathrm{m}}}\frac{qC_c(d_p)}{3\pi\mu Z} \quad . \qquad (8)$$

Here d_p *denotes the mobility diameter,* m_g *the mass of a carrier gas molecule and m the mass of the particle. q is the number of the electrical charges in the particle, μ is the dynamic viscosity of air and Z the electric mobility of the particle.* C_c *is the slip correction factor taking into account non-continuum effects, which become important at small sizes. Note that in earlier studies (e.g. Kulmala et al., 2013) mobilities have been converted to diameters according to the original form of Stokes-Millikan equation, which does not include the mass-dependent factor on the right-hand side of Eq. (8).*

Furthermore, all the figures, tables and the values mentioned in the text that were affected by the size-mobility conversion were replaced with new ones. However, the results did not change significantly, and the change of Eq. (8) affected mainly recombination rates and recombination product concentrations in the smallest size classes.

It is a good point that the mobility-size relation may be different for neutral and charged particles. However, we do not think that the effect of polarization on the mobility should necessarily be taken into account in our analysis as we perform the mobility-size conversion only for recombination products that are assumed to be electrically neutral.

4. It is not clear how the rjk are evaluated when the size range shown in Table 3 do not fall nicely within one of the size ranges shown in Table 4. For example, the upper and lower sizes of the recombination products of N3+P3 are 1.20 and 1.42 nm, respectively. How they will be distributed between two size ranges which is separated at 1.3 nm.

The factor r_{jk} was determined by calculating how big fraction of the size range of recombination products overlaps with different size classes. For example, in the collision between N3 and P3 (for which the lower and upper sizes of the recombination products are 1.09 and 1.35 nm when using the new mobility-size conversion), the factor is (1.1-1.09)/(1.35-1.09)=0.0385 for the size class of 0.9–1.1 nm, (1.3-1.1)/(1.35-1.09)=0.7692 for the size class of 1.1–1.3 nm, and (1.35-1.3)/(1.35-1.09)= 0.1923 for the size class of 1.3–1.5 nm. To clarify this issue, we added the following sentence to the section 2.2.2 (page 20817, line 25 in the ACPD version):

The value for the factor r_{ijk} can be resolved for each ion pair $N_j^+N_k^-$ by calculating how big fraction of the size range of their recombination products overlaps with size class i.

5. Page 9 line 1-4. Authors may be able to discuss more on the difference between their results and Manninen et al (2009a). After reading this paper I thought that the results of Manninen et al (2009a) most likely over-estimated the concentration of recombination products if they did not account for the particle growth.

In fact, Manninen et al. (2009a) did not study the concentration of recombination products but only recombination rate, which is not affected by the particle growth. However, to add some discussion about the results of earlier studies neglecting the effect of condensational growth, we added the following sentence to the end of the section 3.2 (page 20822, line 23 in the ACPD version):

In fact, it seems that if the effect of condensational growth is neglected but the value of the coefficient λ is still assumed to equal 1, as has been done for example by Lehtipalo et al. (2009), the concentration of recombination products is probably overestimated.

PURE TECHNICAL CORRECTIONS

1. Page 8 line 2, “to” is repeated twice

This correction was made.

2. The contents of Figure 6(a) and 6(b) probably needs to be switched. Figure 6(a) which accounts for the effect of particle growth show larger concentrations of the recombination products, which is inconsistent with the arguments in the paper.

Actually, this is not the case. The reason for the obtained lower concentrations when the growth is not taken into account is that in that case the coefficient λ, describing the fraction of stable recombination products, is not assumed to equal 1, as is done when the effect of growth is considered. This is explained in the end of the section 3.2, which is hopefully now clearer after adding the sentence related to the 5th comment. The end of the section now reads (page 20822, line 18):

The fraction of recombination products appeared to have its maximum at smaller sizes than when the effect of condensational growth was taken into account (Fig. 3). The median values of the fraction were also clearly lower, varying between 0.3% and 5%. This is mainly due to the fact that in this analysis the coefficient λ was not assumed to equal 1, as was done when the condensational growth term was included in the calculations. In fact, it seems that if the effect of condensational growth is neglected but the value of the coefficient λ is still assumed to equal 1, as has been done for example by Lehtipalo et al. (2009), the concentration of recombination products is probably overestimated.

In addition, the caption of Figure 6 was also modified to make this issue clearer (page 20837 in the ACPD version):

Figure 6. The percentage of recombination products of all neutral clusters in different size classes a) when assuming that the cluster growth rate increases more slowly with the increasing size than shown by experimental data b) when the effect of condensational growth is neglected and the coefficient λ is not assumed to equal 1. The red lines show the medians, the blue boxes indicate the 25th and 75th percentiles, and the vertical bars show the 5th and 95th percentiles.