A method to determine the size distribution of recombination products from atmospheric measurements

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Ion-ion recombination is a process where a neutral cluster is formed in a collision between two oppositely charged clusters. Based on atmospheric measurements, recombination has been estimated to have only a minor role in new particle formation in boreal forest (Kulmala *et al*., 2007; 2013). However, some model studies propose that recombination could be more important than indicated by the measurements (Yu and Turco 2008). In this work we present the method developed by Kontkanen *et al*. (2013) to determine the size distribution of recombination products from atmospheric measurements. We also apply the method to data measured in Hyytiälä, Finland.

The concentration of recombination products N_{rec} in a size range i can be estimated from the equation:

$$\frac{dN_{rec,i}}{dt} = \lambda_i \alpha \sum_{j,k} r_{jk} N_j^+ N_k^- - CoagS_i N_{rec,i} \, . \qquad (1)$$

Here λ_i denotes the fraction of stable recombination products and α is the ion-ion recombination coefficient. N_j^+ and N_k^- refer to the concentrations of positive and negative ions in the size ranges j and k, and r_{jk} tells which fraction of the recombination products formed in their collisions end up in the size class i. $CoagS_i$ denotes the coagulation sink. Hence, Eq. (1) includes the terms representing the production of neutral clusters in collisions between two oppositely charged ions and the loss of them due to coagulation. The sources and sinks of neutral clusters due to charging, condensational growth and break-ups of larger clusters are neglected. In steady state Eq. (1) can be written as

$$N_{rec,i} = \frac{\lambda_i \alpha \sum_{j,k} r_{jk} N_j^+ N_k^-}{CoagS_i} \, . \qquad (2)$$

The production rate of recombination products to a size range i can be obtained from ion mobility distributions measured with the NAIS (Neutral cluster and Air Ion Spectrometer; Manninen *et al*. 2009). First, we may convert the mobility ranges of NAIS channels to mass ranges. Thereafter, we can calculate the masses of recombination products formed in collisions between ions from different channels. Finally, we may convert the masses of recombination products to mobility diameters and thus determine the production rate of recombination products to the examined size range i.

In earlier studies the fraction of stable recombination products, λ_i, has been assumed to equal unity. However, we can estimate the maximum value for the coefficient, $\lambda_{max,i}$, from measurements. This can be done by stating that the concentration of recombination products in a size range i cannot exceed the concentration of all neutral clusters, which can be obtained by subtracting ion concentration from the total concentration.

To asses the role of recombination in the dynamics of sub-2nm clusters, we applied our method to data measured in Hyytiälä, Finland, during spring 2011. The total cluster concentration in six sub-2nm size classes was measured with the PSM (Particle Size Magnifier; Vanhanen et al., 2011) and ion concentration in the same size classes was measured with the NAIS.

The production rate and the concentration of recombination products were calculated for six sub-2nm size classes (0.9–1.1 nm, 1.1–1.3 nm, 1.3–1.5 nm, 1.5–1.7 nm, 1.7–1.9 nm, and 1.9–2.1 nm). The median production rates of recombination products were observed to vary between 2×10^{-3} cm^{-3} s^{-1} and 8×10^{-2} $cm^{-3}s^{-1}$ in these size classes. The median concentrations of recombination products varied between 2 cm^{-3} and 33 cm^{-3}. Both the production rate and the concentration of recombination products were lowest in the smallest (0.9–1.1 nm) and the largest (1.9–2.1 nm) size classes, and highest in the size classes between them.

The fraction of recombination products of all neutral clusters was also examined. The fraction was lowest in the smallest size class, in which the median fraction was 7×10^{-4}. In other size classes the median fraction was between 0.04 and 0.11. Thus, it seems that on average only a small proportion of all neutral clusters in Hyytiälä are formed in ion-ion recombination. This result is in agreement with the findings of earlier studies estimating the concentration of recombination products from atmospheric measurements.

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