OVERVIEW ON SMALL IONS IN THE ATMOSPHERE

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INTRODUCTION

In recent decades, secondary aerosol particle formation has been studied intensively (Kulmala et al., 2004; Kulmala and Kerminen, 2008). Thus, different formation and growth mechanisms have been proposed for the very first steps of the process: homogeneous-, heterogeneous-, ion-induced- and kinetic nucleation, and activation type cluster growth. Ion-induced particle formation is limited by the ion production rate, which typically is around 10 ion pairs cm⁻³ s⁻¹ in the boundary layer over the ground. The ion production rate has strong spatial and temporal dependence. Indeed, ionisation mechanisms change with altitude: radon and gamma radiation from the ground and galactic cosmic rays dominate close to the Earth’s surface, while higher in the free troposphere cosmic rays become the main driving factor. Radon decay produces typically up to 4 out of 10 ion pairs cm⁻³ s⁻¹ in the boundary layer. The maximum ion production rate by galactic cosmic rays is 35 ion pairs cm⁻³ s⁻¹ at the altitude of 10-15 km, while the minimum is only ca. 2 cm⁻³ s⁻¹ at the ground level (Bazilevskaya et al., 2008). The later is the total ionisation rate over the sea surface, where the ionisation by radon decay and gamma radiation is completely prevented. Furthermore, in winter the radon and gamma radiation are reduced by the snow cover. Radon is a gas and thus accumulates during night time inversion causing higher ion production rate than during day time when mixing is more efficient.

Here we present a short review of the observations of small ion (< 3 nm in diameter). Our primary interest was in the small ion concentration and size distribution spatial and temporal variation. In addition to that the secondary interest was in the connection between small ions and new particle formation. This review is based on over 100 publications and the observations utilised were made all over the world: Europe, Africa, America, Asia, Antarctica and Australia.

OBSERVATIONS

The history of the measurements of electricity in the atmosphere began with the studies of thunderstorms and atmosphere’s electrical conductivity in the end 19th century, as reviewed by Flagan (1998). Already in the beginning of the 20th century, gas ion and aerosol electrical measurements began by many scientists. The instrumental development has enabled the very high time and size resolution in mobility/size distribution measurements (Fig. 1).
Based on previous studies, small ions have been observed everywhere and all the time: in rural and urban conditions, at high altitudes and close to the sea surface. Typically, the small ion concentrations varied in the range of 100-2000 cm$^{-3}$ in both polarities. As one could expect, the concentrations were dependent on the measurement site and some difference between the polarities was observed. There is also a possibility that instrumental bias has an effect on the results of this kind of overview. Due to the differences in chemical composition, positive small ions have larger mean size than negative ones.

Usually, particle formation events begin from the small ion sizes indicating at least some contribution of ions in the process (Fig. 1). However, sometimes there is a gap (around 3 nm) in the size distribution between small ions and larger particles (in one or the other polarity), which indicates that neutral mechanisms are more important than ion-induced mechanisms for that polarity. However, there is also a possibility that new particle formation event takes place at some distance away and already growing particles drift to the measurement site. New particle formation events typically take place after sunrise since they are driven by the high concentrations of nucleating and condensing vapours, and low coagulation sink due to the pre-existing aerosol. However, some observations on small ion activation during the night have also been reported.

Based on observations, the formation rates of 2-nm particles by ion-induced mechanisms are typically in the order of ≤1 cm$^{-3}$s$^{-1}$, while the total 2-nm particle formation rate varies between 0.001-60 cm$^{-3}$s$^{-1}$. It has been observed that with small total 2-nm particle formation rates the ion-induced mechanisms can
explain the new particle formation completely, while, with high total formation rate neutral mechanisms dominate (e.g. Kulmala et al., 2010). However, the contribution may also vary within an individual nucleation burst (Laakso et al., 2007). In boreal forest, the average contribution of ions in particle formation rate of 2-nm particles is estimated to be 10% (e.g. Kulmala et al., 2010).

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