Overview on the observations of small ions in the atmosphere

Hirsikko, Anne[1], Kulmala, Markku[1], Nieminen, Tuomo[1], Manninen, Hanna[1], Gagné, Stéphanie[1], Lehtipalo, Katrianne[1], Laakso, Lauri[2,1], Vana, Marko[3], Hõrrak, Urmas[3], Mirme, Aadu[3], Mirme, Sander[3], Tammet, Hannes[3] and Kerminen, Veli-Matti[4]

[1]Department of Physics, University of Helsinki, P.O. BOX 64, 00014 University of Helsinki, Finland
[2]School of Physical and Chemical Sciences, North-West University, Potchestroom, Republic of South Africa.
[3]Institute of Physics, University of Tartu, 18 Ülikooli Str., 50090 Tartu, Estonia
[4]Finnish Meteorological Institute, Research and Development, P.O. BOX 503, FI-00101, Finland

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The first steps of new particle formation (NPF) have been studied intensively in recent years. Different NPF and growth mechanisms have been proposed and investigated, i.e. homogeneous-, heterogeneous-, ion-induced- and kinetic nucleation, and activation type cluster growth. Particle formation by ion-induced mechanisms is limited by the ion production rate, which typically is around 10 ion pairs $cm^{-3}s^{-1}$ in the boundary layer. Some higher values have also been observed depending on the measurement location. 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 0-4 out of 10 ion pairs $cm^{-3}s^{-1}$ in the boundary layer. In winter the radon and gamma radiation are reduced by the snow cover. The maximum ion production rate by galactic cosmic rays only is 35 ion pairs $cm^{-3}s^{-1}$ at the altitude of 10-15 km, while the minimum is ca. 2 $cm^{-3}s^{-1}$ at the ground level (Bazilevskaya et al., 2008).

In our study more than 100 publications about the observations of small ions (< 3 nm in diameter) were overviewed. Our main focus was on small ion concentration and ion size distribution spatial and temporal differences. The secondary focus was on the connection between small ions and NPF. The observations utilised were made all over the world: different sites in Europe, Africa, America, Asia, Antarctica and Australia.

Based on these 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. Typical small ion concentrations vary in the range of 100-2000 cm^{-3} in both polarities. Usually NPF events begin from the small ion sizes indicating at least some contribution of ions in NPF. 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. NPF events typically take place after sunrise. 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 NPF completely, while, with high total NPF 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 NPF rate of 2-nm particles is estimated to be 10 % (e.g. Kulmala et al., 2010).

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