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Size distributions of atmospheric ions inside clouds and in cloud-free air at a remote continental site

Heikki Lihavainen[1)], Mika Komppula[1)], Veli-Matti Kerminen[1)], Heikki Järvinen[1)], Yrjö Viisanen[1)], Kari Lehtinen[2)], Marko Vana[3)4)] and Markku Kulmala[3)]

[1)] *Finnish Meteorological Institute, Research and Development, P.O. Box 503, FI-00101 Helsinki, Finland*
[2)] *Finnish Meteorological Institute and University of Kuopio, P.O. Box 1627, FI-70211 Kuopio, Finland*
[3)] *Department of Physical Sciences, P.O. Box 64, FI-00014 University of Helsinki, Finland*
[4)] *Institute of Environmental Physics, University of Tartu, Ülikooli 18, Tartu 50090, Estonia*

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During the late autumn 2004, aerosol and air ion number size distributions inside and outside clouds and cloud droplet number size spectra were measured in Pallas, northern Finland. The concentrations of cluster ions (air ions with a diameter < 1.6 nm) were substantially lower, roughly by an order of magnitude, inside clouds as compared with cloud-free air. The observed concentration levels of cluster ions could be explained by a source rate of a few ion pairs per second. The main sink for cluster ions was the cloud droplet population during the cloudy periods and the ion-ion recombination in cloud-free air. Very few intermediate ions (1.6–7.4 nm diameter) were present during the cloudy periods, indicating that processes capable of generating intermediate ions were rather inactive inside clouds during the measurement campaign.

Introduction

Air ions have been investigated for several decades due to their important role in atmospheric electricity and associated cloud processes (Harrison and Carslaw 2003, and references therein). More recently, interest in air ions has increased further after the findings that they may be involved in the atmospheric aerosol formation, and that they provide the only means for measuring the very initial steps of aerosol formation processes at the moment (Horrak *et al*. 1998, Yu and Turco 2000, Kulmala *et al*. 2004, Laakso *et al*. 2004, Lovejoy *et al*. 2004, Vana *et al*. 2004, Hirsikko *et al*. 2005, Eisele *et al*. 2006).

The ions with most relevance for the aerosol formation are the so-called "cluster ions" having a mobility > 0.5 $cm^2\ V^{-1}\ s^{-1}$ (corresponding roughly to particle diameters < 1.6 nm) and "intermediate ions" having a mobility in the range 0.034–0.5 $cm^2\ V^{-1}\ s^{-1}$ (1.6–7.4 nm) (Horrak *et al*. 2003). Air ions have been measured in several different locations and atmospheric conditions but practically no information on their concentrations and mobility/size distributions near or inside clouds is available. The goal of

this paper is to provide such data and to interpret these observations with regard to our current understanding on atmospheric ion and aerosol dynamics. The data set is based on the measurements that were carried out in the northern Finland as part of the First Pallas Cloud Experiment (First PaCE) in autumn 2004.

Description of measurements

Measurements were carried out in the Pallas GAW (Global Atmosphere Watch) station hosted by the Finnish Meteorological Institute (Hatakka *et al*. 2003) and located in the northern Finland. The two measuring sites Sammaltunturi (67°58´N, 24°07´E) and Matorova (68°00´N, 24°14´E) are six kilometres apart and at different altitudes (565 and 340 m above sea level, respectively). The higher-altitude station, Sammaltunturi, is inside clouds during 10% of all days, while the Matorova station is almost always below the cloud layer. A more detailed description of the measurement approach can be found in Komppula *et al*. (2005).

The mobility distribution of air ions (naturally charged clusters and aerosol particles) was measured in the range of 0.0013–3.2 $cm^2\ V^{-1}\ s^{-1}$ using an Air Ion Spectrometer (AIS, manufactured by AIREL Ltd., Estonia) (Mirme *et al*. 2007). The AIS consists of two identical cylindrical aspiration-type differential mobility analyzers, one for positive and one for negative ion measurements. The collecting electrode of each mobility analyzer is divided into 21 electrically isolated sections, each of which is provided with an individual electrometrical amplifier for the measurement of electrical current carried by ions of different mobilities. The sample air containing ions (the flow rate through each analyzer is 500 $cm^3\ s^{-1}$) is sucked into the mobility analyzer through an electronically controlled electrostatic filter (switched on/off). A closed inlet is used for the verification of the offset level and the noise of electrometrical amplifiers. Both mobility analyzers have a closed-loop of clean sheath air. The unipolar charging of aerosol particles in corona chargers and subsequent removal of charged particles by electrostatic filtration is used to create the clean sheath airflow of 1000 $cm^3\ s^{-1}$. The ion mobility distribution measurements were conducted at the Sammaltunturi station. The corresponding size distribution range of 0.34–40 nm is obtained using the concept of mass diameter developed by Tammet (1995). It has not been tested how the AIS electrometers are influenced by the changes in relative humidity. However, if there is some leakage of signal due to high humidity in cloud, the measured signals should have high noise level due to the random character of leakage. In these measurements this was not the case and it is assumed that changes in relative humidity did not affect the AIS measurements.

Similar DMPS (Differential Mobility Particle Sizer; e.g. Aalto *et al*. 2001) systems are employed at both Sammaltunturi and Matorova station for measuring the dry particle number size distribution in the diameter range 7–500 nm. With this setup, the cloud interstitial particle size spectrum and a nearby out-of-cloud particle size spectrum were measured simultaneously. The number concentration and fraction of activated particles for all size bins could be estimated by comparing the in-cloud and out-of-cloud size spectra. The two DMPS systems were calibrated against each other, in addition to which total particle number concentrations measured by the DMPS systems were compared with those measured with a Condensation Particle Counter.

Cloud droplet number size distributions in the diameter range 2–47 μm were measured with a FSSP (Forward Scattering Spectrometer Probe, Particle Measuring System Inc. USA). The FSSP was mounted on a rotating platform with its inlet always pointing to the wind. The apparatus was placed on the top of the Sammaltunturi station building.

Classification of in-cloud/cloud-free air was based on three independent observations: web camera photos, visibility measurements and DMPS data. In the DMPS data, particles larger than about 100 nm in diameter are almost completely absent during cloudy periods. An upper limit of 500 m for visibility was selected as a criterion for the in-cloud air, in addition to which the occurrence of the cloud was confirmed using web camera photos. All the three criteria had to be fulfilled before the data was classified as in-cloud air. Cloud-free air had to have visibility

larger than 20 000 meters. The above limits were allowed to be occasionally exceeded for a few minutes during otherwise solid in-cloud or cloud-free periods. The FSSP was not used in the classification because it was not running continuously. The periods between cloud-free and in-cloud air masses, as well as other unclear situations, were classified as "grey area" and were omitted in further analyses. Fractions of in-cloud, cloud-free and grey area during the campaign period were 50%, 35% and 15%, respectively

Results and discussion

General character of measured air masses

The campaign covered the period between 20 October and 9 November 2004. The meteorological conditions at the measurement site during the campaign were affected by passages of several depressions from the south-west with associated overcast and variable winds for most of the time. Higher pressure and fair skies were present only on few occasions. The ambient temperature was –3 °C on average and varied between –8 °C and +5 °C.

The overall average particle number concentration, as measured at the Matorova station, was 260 cm^{-3}. The hourly average particle number concentration varied between 30 and 1200 cm^{-3} depending on the air mass history. In general, low particle number concentrations were related to air masses coming almost directly from the Arctic Ocean, whereas the highest particle number concentrations were associated with continental air masses. The cloud droplet number concentration correlated positively with the total particle number concentration, averaging at 85 cm^{-3} and ranging from 25 to 250 cm^{-3}. The geometric mean diameter of cloud droplets was 16 μm and varied between 6 and 27 μm.

Ion concentrations and size distributions

During the campaign, the average ion concentrations were 505 and 617 cm^{-3} for positive and negative ions, respectively. These values are in agreement with those measured earlier in Estonia and southern Finland (Horrak *et al*. 2003, Hirsikko *et al*. 2005). The variability of the one-hour average ion concentrations was relatively large (Table 1), especially when compared with many earlier studies (e.g. Horrak *et al*. 2003, Hirsikko *et al*. 2005). The main reason for this variability was that the measurements station was inside a cloud for a large fraction of time during the campaign. On average, total ion concentrations were 5–6 times higher in cloud-free air in comparison with in-cloud air.

During cloud-free periods, the size distributions of both positive and negative ions were dominated practically always by a relatively narrow mode peaking at about 1 nm (Fig. 1). Similar clusters ion modes had been measured earlier in a rural area site in Estonia (Horrak *et al*. 2003), as well as at a boreal forest site in the southern Finland (Laakso *et al*. 2004, Hirsikko *et al*. 2005). Very few intermediate ions were present, except during the few periods indicative of new-particle formation and growth. A broad yet rather weak large ion mode could usually be observed in the size range of 10–40 nm.

During in-cloud periods, the positive and

Table 1. Concentrations (mean ± SD (range); ions cm^{-3}) of positive and negative cluster ions (diameter < 1.6 nm), intermediate ions (1.6–7.4 nm), large ions (7.4–40 nm) and all air ions together during clear air and in-cloud periods. Reported ranges are based on one-hour average data.

	Positive ions		Negative ions	
	clear air	in-cloud	clear air	in-cloud
Cluster ions	973 ± 346 (347–1754)	135 ± 71 (35–485)	1182 ± 360 (418–1978)	175 ± 91 (45–595)
Intermediate ions	10 ± 14 (< 97)	3 ± 1 (< 11)	19 ± 25 (< 120)	4 ± 4 (< 22)
Large ions	27 ± 28 (3–145)	38 ± 30 (4–193)	22 ± 21 (3–116)	32 ± 26 (3–153)
All sizes	1007 ± 370 (363–1813)	175 ± 72 (52–494)	1221 ± 390 (429–2070)	209 ± 92 (58–602)

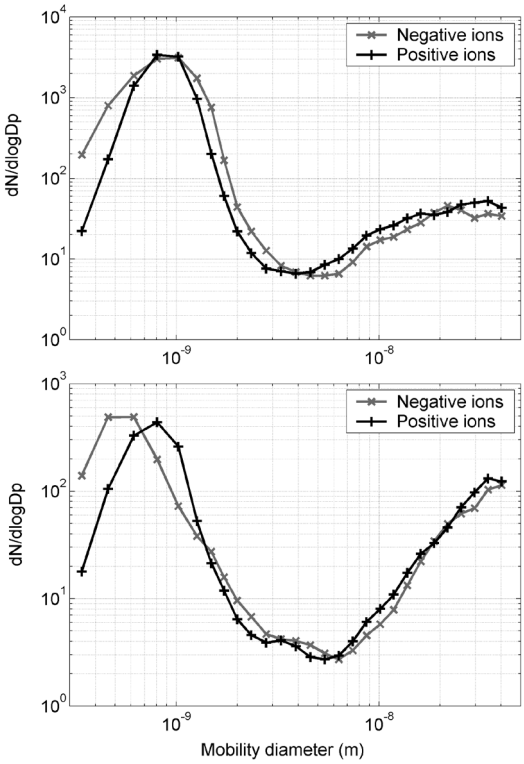

Fig. 1. Average size distributions of positive and negative ions in cloud-free air (top) and inside clouds (bottom).

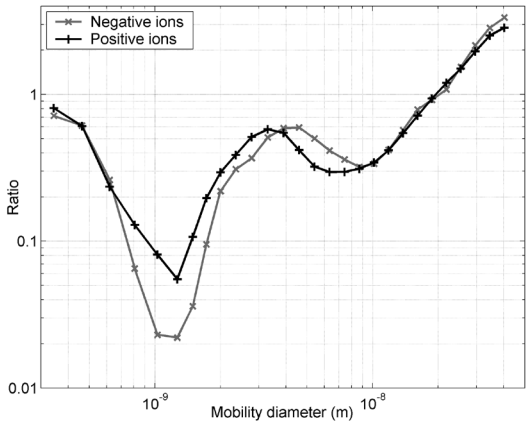

Fig. 2. The ratio of air ion concentrations between the in-cloud and clear air periods as a function of ion mobility diameter.

negative cluster ion modes were always rather weak and they peaked at clearly different sizes (Fig. 1). Concentrations of intermediate ions were extremely low inside clouds, but a steep increase in ion concentrations with increasing particle size above 10 nm diameter was usually measured.

The average ion concentration ratio between the in-cloud and cloud-free air was well below unity for cluster ions (Fig. 2). This feature can be ascribed to the large sink of cluster ions caused by cloud droplets, making the lifetime of these ions very short (typically a few seconds, *see* analyses below) inside clouds as compared with cloud-free air. Above 20 nm, particles are expected to be close to charge equilibrium and their equilibrium charged fraction increases roughly proportional to their ambient diameter (e.g. Hoppel and Frick 1986). Particles with dry diameters below 40 nm are usually too small to be activated into cloud droplets, yet their ambient sizes are expected to be larger by a factor of 2–5 inside clouds compared with those in cloud-free air. This is the probable explanation for the observation that, on average, concentrations of ions inside clouds exceeded those in cloud-free air in the dry particle size range of 20–40 nm (Fig. 2).

In order to provide some insight into the dynamical changes in air ion populations, two measurement days are considered next in more detail. The first one is 26 October when the station was inside a cloud for the whole day. There was a depression to the west of the area with prevailing southerly winds at the site. Overcast in the area was due to a weak occlusion. Presence of clouds at the site can be seen very clearly from the DMPS data, showing practically no particles in the size range of 100–500 nm (Fig. 3), and from the cloud droplet number concentration measured with the FSSP and calculated from the difference in particle number size distributions between inside cloud (Sammaltunturi) station and outside cloud station (Matorova) (Komppula *et al*. 2005). The DMPS data reveal a marked cloud interstitial particle mode. This mode was centered initially at about 20–30 nm, after which it grew gradually in size during the rest of the day. The number concentration of particles in this mode reached a maximum of about 500 cm^{-3} during the morning hours and decreased then to values below 200 cm^{-3} by midnight. The ion size distributions were dominated by a mode in the

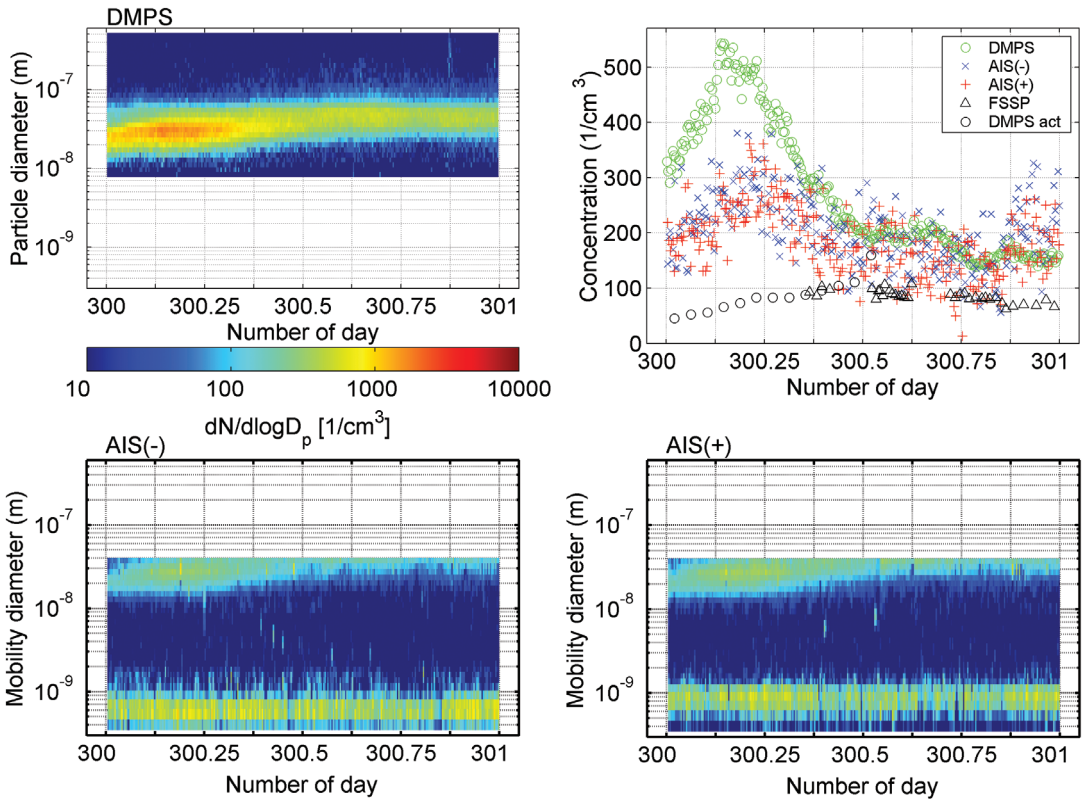

Fig. 3. Measured aerosol particle (DMPS) and air ion (AIS+ and AIS–) size distributions, along with total particle, air ion and cloud droplet (FSSP and DMPSact) number concentrations, as a function of time during 26 October 2004. The station was inside clouds the whole day.

size range of 10–40 nm. Both the location and magnitude of this mode tracked closely the corresponding aerosol particle mode measured by the DMPS, giving strong indications that these ions modes originated from the coagulation of cluster ions with cloud interstitial particles. Both positive and negative ions displayed another, rather weak mode centering below 1 nm. The total concentrations of these cluster ions were very low during the whole day, averaging at 110 cm^{-3} and 140 cm^{-3} for positive and negative ions, respectively.

The second measurement day of special attention is 28 October. During that day, the site was inside cloud until the midday when the cloud suddenly disappeared (Fig. 4). The overcast and south-westerly winds early on this day were due to a small depression and an occlusion to the north of the site. The depression moved eastward during the day and a high pressure ridge developed to the south-west of the site with associated fair skies and turning of winds to the north-west. The transition from in-cloud to cloud-free air can be seen in both the DMPS and the AIS data. The DMPS data displayed a sudden appearance of particles in the size range of 100–500 nm as soon as the cloud disappeared. Although the recent history of these particles is unknown, at least a fraction of them can be ascribed to residuals from evaporating cloud droplets. The most striking feature associated with the in-cloud to cloud-free transition was the immediate increase of the cluster ion concentrations by almost a factor of ten compared with the respective concentration inside the cloud. Similarly, very sudden changes in cluster ion concentration could be seen on many other days as well when a transition from in-cloud to cloud-free air, or vice versa, took place.

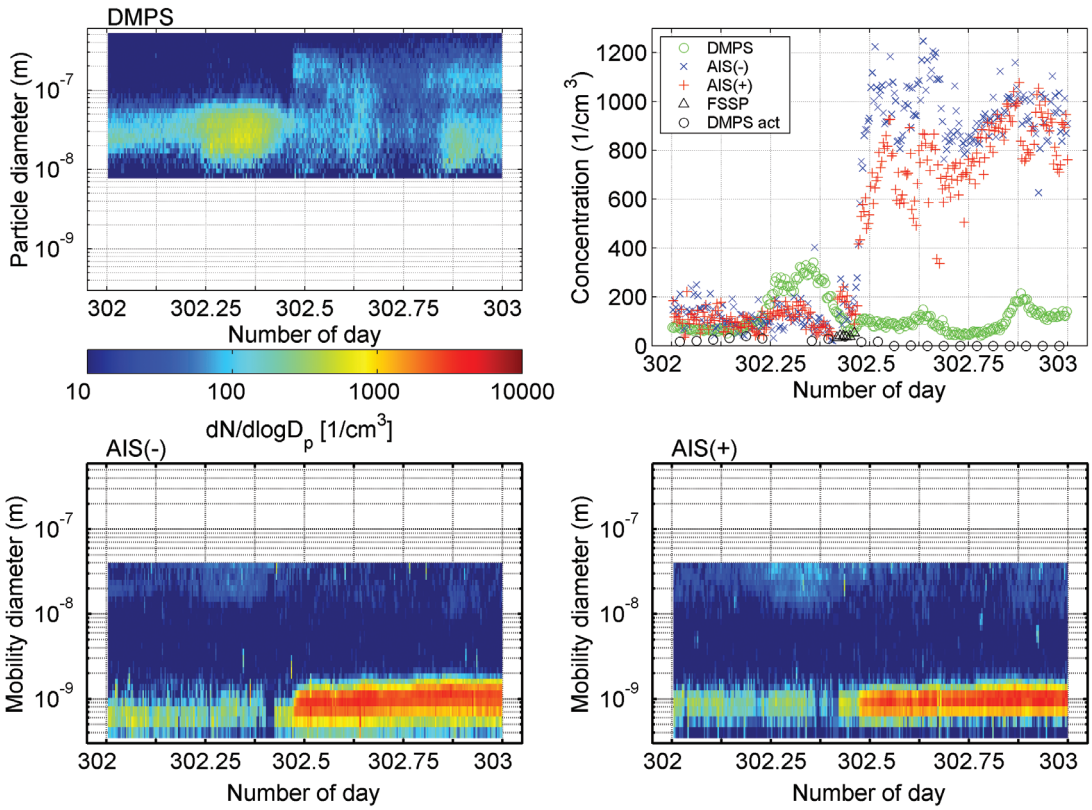

Fig. 4. Same as Fig. 3, except for 28 October 2004. The cloud disappeared just before the midday at around 302.47.

Sources and sinks for cluster ions

The concentration of cluster ions, n (positive or negative), can be estimated from the following balance equation (Schonland 1953):

$$\frac{dn}{dt} = Q - \alpha n^2 - S_{\text{Coag}} \times n - S_{\text{Cloud}} \times n \qquad (1)$$

The first term on the right-hand side (Q) represents the ion source rate. The second term is the loss rate of ions due to recombination (α being the ion-ion recombination coefficient), i.e. collisions between positive and negative ions. The third term is the loss rate due to collisions with aerosol particles, with coagulation sink (S_{Coag}) being the rate coefficient depending on the background aerosol size distribution. The last term is the loss rate due to collisions with cloud droplets, with cloud sink (S_{Cloud}) being a function of the cloud droplet size distribution. S_{Coag} and S_{Cloud} are estimated from measured aerosol and cloud drop distributions using the Brownian coagulation theory with the Fuchs' coagulation coefficient.

Scale analysis of the different loss terms in equation 1 is considered next using measured parameter values. In clear air cases, the average value of n is roughly 10^3 cm^{-3} (Table 1). The sink S_{Coag} onto background particles can be integrated from the measured particle number size distributions on clear days, being approximately 2×10^{-4} s^{-1}. The ion-ion recombination coefficient is roughly 2×10^{-6} cm^3 s^{-1} (Hoppel and Frick 1986). With these values, the magnitude of the recombination loss term is 1 cm^{-3} s^{-1} and the magnitude of the coagulation-with-aerosols loss term is 0.1 cm^{-3} s^{-1}. Thus, when estimating ion concentrations on cloud-free days, to first order, the coagulation loss term can be neglected. For cloudy cases, n and S_{Coag} are on average roughly 200 cm^{-3} and 8×10^{-4} s^{-1}, respectively. The cloud sink can be integrated from the mean cloud droplet distribution, resulting in a value of about

0.1 s^{-1}. The magnitudes of the three loss terms, due to recombination, aerosol loss and cloud loss are thus of the order of 0.1, 0.1 and 10 cm^{-3} s^{-1}, respectively. Hence in cloudy cases the other two loss terms are negligible and only scavenging by cloud droplets needs to be considered.

Next, let us investigate, given the conditions of our measurements for cloud droplets and background aerosol, what kind of steady-state ion concentrations are predicted by Eq. 1. For the cloudy conditions we have, assuming an ion source rate of 5 cm^{-3} s^{-1},

$$n \approx \frac{Q}{S_{\text{Cloud}}} \approx \frac{5\ \text{cm}^{-3}\ \text{s}^{-1}}{0.1\,\text{s}^{-1}} = 50\ \text{cm}^{-3}$$

and for the clear conditions

$$n \approx \sqrt{\frac{Q}{\alpha}} \approx \sqrt{\frac{5\ \text{cm}^{-3}\ \text{s}^{-1}}{2\times10^{-6}\ \text{cm}^{3}\ \text{s}^{-1}}} \approx 1500\ \text{cm}^{-3}$$

The results are within a factor of four of what is observed on average (*see* Table 1), demonstrating that a simple steady-state analysis can qualitative predict the reduction in ion concentrations in cloudy conditions.

It is interesting to note that the high ion concentration values of approximately 1000 cm^{-3} in clear conditions result in recombination rates of above 1 cm^{-3} s^{-1}. Since recombination is a source of neutral clusters, this phenomenon may be an important source of new particles under these conditions, provided that the neutral clusters formed by recombination are stable.

Summary and conclusions

The measurements conducted at the two sites in Pallas provided a unique opportunity to investigate the size distributions of air ions inside clouds and to compare them with the corresponding size distributions measured during cloud-free periods. Further insight into the dynamics of the air ion population was obtained from the cloud droplet number size distribution measurements, as well as from the simultaneous particle number size distribution measurements both inside and outside clouds.

The concentrations of cluster ions (air ions with a diameter < 1.6 nm) were substantially lower inside clouds as compared with cloud-free air, the average concentration difference being almost an order of magnitude. Scale analysis and steady-state ion balance calculations showed that the main sink of cluster ions was the population of cloud droplets during cloudy periods and ion-ion recombination in cloud-free air. The observed concentration levels of cluster ions could be explained by a source rate of a few ion pairs per second, both inside cloud and in cloud-free air. The success in calculating cluster ion concentrations demonstrates that reliable air ion size distribution measurements inside water clouds are possible, and that the production rate of cluster ions inside clouds does not significantly differ from that in cloud-free air.

Very few intermediate ions (1.6–7.4 nm) were present during the cloudy periods, indicating that the processes capable of generating intermediate ions were rather inactive inside clouds during the measurement campaign. In contrast, the average concentrations of 20–40 nm air ions were slightly higher inside clouds than in cloud-free air. This finding could be explained by the larger ambient size, and thus by the larger equilibrium charged fraction, of unactivated Aitken mode particles inside clouds compared with particles having similar dry sizes in cloud-free air.

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