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Size distributions of atmospheric ions in the Baltic Sea region

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Number size distributions of air ions and aerosol particles were measured at three sites in the Baltic Sea region in spring 2004. One site was on the island of Utö in the Baltic Sea and the two other sites, Hyytiälä and Tahkuse, had a more continental location not far away from the coast of the Baltic Sea. The concentrations of cluster ions (air ions with a diameter < 1.6 nm) were about three times smaller at the Utö island as compared with those at the Hyytiälä mainland site in Finland, although the particle concentrations (i.e. ion sink) were at about the same level at these two sites. Generally, the Utö island had the lowest air-ion concentration probably due to weaker sources for ions than the other two more continentally-located stations. Intermediate ion concentrations (1.6–7 nm diameter) were generally low, even though they reached several hundreds cm^{-3} during nucleation episodes. Charging probabilities of < 8 nm particles were found to be close to the steady state in all the three sites, suggesting that ion-induced nucleation was not playing a major role during this time period.

Introduction

The formation and growth of ultrafine aerosol particles in the atmosphere has been studied for the last 10 years at many locations around the world (e.g. Birmili *et al*. 2003, Tunved *et al*. 2003, Kulmala *et al*. 2004a), and evidence on the participation of these particle into cloud droplet activation was obtained (Kerminen *et al*. 2005). Despite the frequent observations of particle formation events, the microphysical mechanisms responsible for this phenomenon have remained unclear mainly because of instrumental limitations. At the moment we are only able to detect neutral particles larger than about 3 nm in diameter. Recently, the interest in air ions has increased because ions provide the only means for measuring the very initial steps of atmospheric aerosol formation (down to about 0.4 nm), and because ions themselves may be involved in the aerosol formation process (Hõrrak *et al*. 1994, 1998, 2003, Yu and Turco 2000, 2001, Lee *et al*. 2003, Laakso *et al*. 2004a, 2004b, Lovejoy *et al*. 2004, Vana *et al*. 2004, Kulmala *et al*. 2004a, 2004b, Eisele *et al*. 2006).

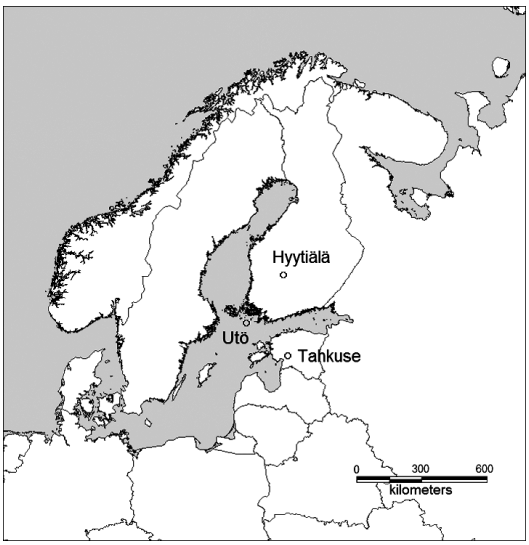

Fig. 1. A map showing the location of the measurement sites.

Tropospheric air-ions (here 0.35–40 nm in diameter) make up a very small fraction of ambient air, reaching typically concentrations of the order of 10^2–10^3 cm^{-3}. The ion concentrations are controlled by the competition between their production and loss. The ion production comes from cosmic ray ionization occurring throughout the troposphere, from ionization by gamma radiation from the ground, and from the radioactive decay of compounds such as radon. The two latter processes typically dominate near the ground level over land surfaces (Israël 1970, Hoppel *et al*. 1986, Porstendörfer 1994), whereas cosmic ray ionization dominates over the oceans (Hensen and Van Der Hage 1994). The loss of tropospheric ions is controlled by ion-ion recombination when the aerosol surface area is low and by loss to particle surfaces when the particle surface area is high.

Even very low concentrations of atmospheric ions could initiate the production of a significant number of ion clusters that could eventually grow into new aerosol particles. The knowledge about the behaviour of ion clusters, particles and their charged fraction (air ions) during nucleation events could help us to find out the role of different nucleation mechanisms.

The aim of this paper is to present new ion measurements and comparison of ion data from three measurement sites in the Baltic Sea region (Fig. 1): Utö, an island in Baltic Sea, Hyytiälä in Finland about 150 km from the Baltic Sea, and Tahkuse about 30 km from the coast in Estonia. Our main goal was to investigate the ion size-distributions and new particle formation in the specific surrounding of the Utö island in contrast to the other two sites.

Description of measurements

Measurement sites

The Utö measurement station (59°47´N, 21°23´E, 8 m above the sea level) is located on a small island in the Baltic Sea about 60 kilometres from the Finnish coast and more than 10 km from the nearest islands around. The closest major city Turku, with 175 000 inhabitants, is located about 90 kilometres north-east of Utö. Within a 10-kilometer radius from Utö, 99% of the area is covered by the sea. The area of the rocky and almost treeless island of Utö is less than 1 km^2. There are only few local pollutant sources nearby, such as passing large ships and some houses on the island. Utö has served as a sea-weather station since 1881, whereas air quality measurements started there in 1980. Continuous aerosol measurements have been carried out since 2003.

The Hyytiälä measurement site SMEAR II (Station for Measuring Forest Ecosystem–Atmosphere Relations) is located in southern Finland (61°51´N, 24°17´E, 181 m above the sea level). Hyytiälä is a remote site located about 280 km north-east from Utö and about 150 km from the Baltic Sea coast. The closest major city, Tampere with 200 000 inhabitants, is about 60 kilometres south-west of Hyytiälä. The measuring station is surrounded mainly by a Scots pine forest. The measurements and surroundings of the station have been described in more detail by Vesala *et al*. (1998), Kulmala *et al*. (2001b) and Hari and Kulmala (2005). In addition to particle measurements, continuous measurements of the mobility distributions of atmospheric ions were started in spring 2003.

The Tahkuse Observatory (58°31´N, 24°56´E, 37 m above the sea level) is located in a sparsely-populated rural region, about 30 km northeast from the city of Pärnu, in Estonia (Hõrrak *et al*.

1994). Pärnu, with 52 000 inhabitants, is situated on the coast of the Gulf of Riga in the Baltic Sea. Tahkuse is located about 250 km south-east from the Utö island, and the distance between Tahkuse and Hyytiälä is about 370 km. The first ion measurements at Tahkuse were carried out already in 1985.

Measurements

This paper presents an analysis of observations made during a measurement campaign held in Utö and combines results obtained from simultaneous measurements conducted in Hyytiälä and Tahkuse. The Utö campaign was organized in spring 2004 and it took place between 19 April and 21 May. The focus of the campaign was to investigate the variability of air ion concentrations and new-particle formation in this specific surrounding, a marine site influenced by continental air.

In both Hyytiälä and Utö, the size distributions of air ions (naturally charged clusters and aerosol particles) were measured in the mobility range of 0.0013–3.2 $cm^2\ V^{-1}\ s^{-1}$, corresponding to mobility diameters of 0.35–40 nm, using an Air Ion Spectrometer (AIS, manufactured by AIREL Ltd., Estonia) (Mirme *et al*. 2007). The AIS has two identical cylindrical aspiration-type Differential Mobility Analyzers (DMA), one for positive and the other for negative ion measurements. Naturally-charged particles (cluster ions and aerosol ions) carried by the air flow drift in the radial electric field of the DMA and are deposited on different collector electrodes of the DMA according to their electrical mobilities. Each mobility analyzer has 21 insulated collector electrodes, from which electrometrical amplifiers measure the electric current carried by the ions. The AIS uses a sample flow rate of 500 $cm^3\ s^{-1}$, whereas the sheath air flow rate is 1000 $cm^3\ s^{-1}$ for each analyzer. When the instrument measures the offset level and noise of the amplifiers, particles in the sample air are neutralized and charged by a unipolar corona charger. Then the charged particles are removed from the airflow by an electric filter. When ion concentrations are measured, the corona charger and electric filter are switched off. The two analyzers have separate closed-loop sheath flow arrangements. Additional corona chargers and electric filters clean continuously the sheath air by using the same method described above. The diameter distributions of single charged particles are obtained by utilizing the algorithm developed by Tammet (1995, 1998).

A complex of air ion spectrometers (AIS) installed at Tahkuse covers a mobility range of 0.00041–3.2 $cm^2\ V^{-1}\ s^{-1}$ (Hõrrak *et al*. 2000). The corresponding range of particle diameters is from 0.35 to 77 nm when assuming single charges on particles. The whole range of mobility is logarithmically divided into 20 intervals. Thus each mobility spectrum is commonly presented by 20 concentration fractions. The complex consists of three original multichannel aspiration spectrometers designed according to the principle of the second-order differential mobility analyzer. The sampling height for the air-ion measurements was 2 m in Utö and Hyytiälä and 5 m in Tahkuse.

In addition to ion measurements, aerosol particle number size distributions were measured in all the three sites. In Utö and Hyytiälä DMPS (Differential Mobility Particle Sizer) systems were used and in Tahkuse an EAS (Electrical Aerosol Spectrometer) was used for particle sizing. In Utö, the measured particle size range covered particle diameters from 7 to 500 nm and in Hyytiälä from 3 to 500 nm. The EAS in Tahkuse measured particle sizes from 3 nm to 10 μm (Tammet *et al*. 2002). Weather data were available for all the stations and five-day back trajectories were calculated with the FLEXTRA model (Stohl *et al*. 1995).

Results and discussion

General character of measured air masses

During the campaign, the stations were influenced by air masses quite evenly originating from all directions. Both marine-influenced air masses and on the other hand air masses with a very strong continental influence were experienced. On most of the days all the three stations were influenced by air masses of the same origin.

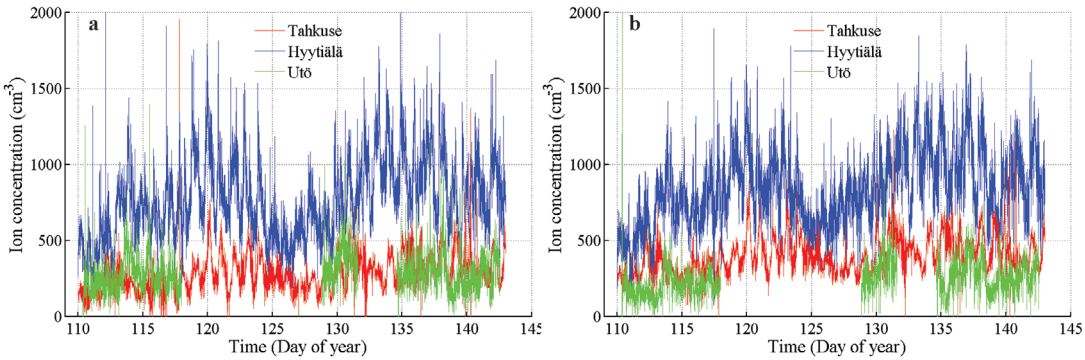

Fig. 2. Time evolution of negative (**a**) and positive (**b**) cluster ion concentrations in the three locations during 19 April–21 May 2004.

This provided a good basis for comparing the sites and for selecting single days with different air mass properties for case studies. Due to relatively close location of the sites, the meteorological conditions were relatively similar at all the sites. During the campaign the average temperatures varied from 7.2 °C in Utö to 10.4 °C in Tahkuse. Even though the average temperatures were close to each other, the daily variation was clearly lowest at the marine Utö site. Wind speeds at the Utö site were on average — and especially on some occasions — higher than at the two continental sites. Earlier studies showed that the variation in meteorological parameters can have an effect on ion concentrations (Hõrrak *et al*. 2003). This matter will be discussed more when comparing the three sites.

Ion concentrations and size distributions

Our measurements at the three sites gave us an opportunity to investigate the variability of air ion concentrations in the Baltic Sea region. In order to understand the formation mechanisms of atmospheric aerosol particles, knowledge about the variability of the ion cluster concentration is important.

Cluster ions represent a distinct and typically quite stable mode in the mobility distribution of air ions. The conventional lower limit of the mobility range of these particles is 0.5 cm^2 V^{-1} s^{-1}, corresponding to a mobility diameter of 1.6 nm (e.g. Hõrrak *et al*. 2000, 2003). Figure 2 shows the time evolution of negative and positive cluster ions at the three sites. The variation of negative and positive ions is quite similar. We can see the highest concentrations in Hyytiälä, and lower concentrations in Tahkuse and Utö. The mean ion concentrations over the whole measuring period are given in Table 1. The concentrations observed at Hyytiälä are in the range of those obtained by the BSMA (Balanced Scanning Mobility Analyzer) for the instrument overlapping period (Hirsikko *et al*. 2005). The smaller concentrations at Tahkuse may be due to higher total aerosol concentrations and thus higher condensation sinks (*see* Fig. 3). At Utö, at the same time, lower cluster ion concentrations may be due a lower source rate (mainly by cosmic radiation) for ions in the clean marine environment and also due to higher wind speeds as compared with those at the continental sites.

Tahkuse had higher aerosol particle number concentrations than Utö and Hyytiälä, whereas the highest variability was observed in Hyytiälä (Fig. 3). The mean total particle number concentration during the measuring period varied from 3700 cm^{-3} at Hyytiälä to 9900 cm^{-3} at Tahkuse (Table 1). This means that Tahkuse had the highest ion sink, 1.0×10^{-2} s^{-1} on average. In practise, the ion sink is linearly proportional to the condensation sink caused by aerosol particles. The average ion sink was lowest at Hyytiälä 0.8×10^{-2} s^{-1}, even though the surrounding forest may introduce an additional sink being about 20% of the total sink as presented by Tammet *et al*. (2006). At Utö and Tahkuse this additional sink would be negligible due non-forested or very sparsely-forested surroundings.

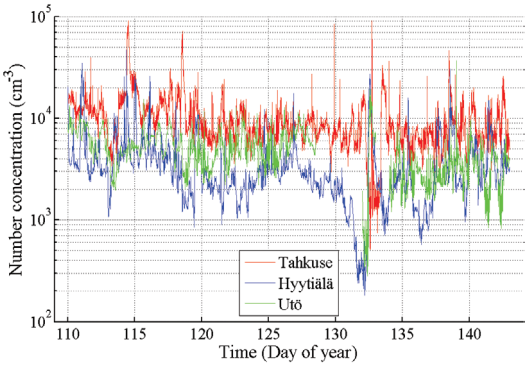

Fig. 3. Time evolution of the total aerosol particle number concentration in the three locations during 19 April–21 May 2004.

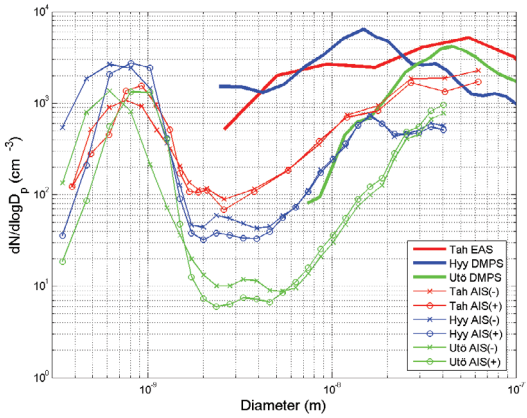

Fig. 4. Daily-mean size distributions of negative and positive air ions and aerosol particles in 16 May 2004 in the three locations.

Another class in the mobility distribution of air ions, beside cluster ions, is the group of aerosol ions with mobilities below 0.5 cm^2 V^{-1} s^{-1}. Here we can separate two groups called intermediate and large ions. The concentrations of intermediate ions in the diameter interval of 1.6–7 nm were generally very low but reached several hundreds cm^{-3} and occasionally > 1000 cm^{-3} during nucleation episodes (Table 1). The mean concentration of light large ions in the diameter interval of 7–22 nm varied from about 50 cm^{-3} at Utö to 400 cm^{-3} at Tahkuse (Table 1).

Figure 4 illustrates typical daily-mean number size distributions of air ions and aerosol particles < 100 nm in diameter at the three locations. At Tahkuse the concentrations of air ions with mobilities below 0.5 cm^2 V^{-1} s^{-1} (diameter > 1.6 nm) were most of the time higher than at Hyytiälä and Utö. Utö had the lowest particle number concentrations in the nucleation mode size range, representing a clean marine environment with fewer sources for new-particle production. Negative cluster ions normally had a concentration peak at slightly smaller sizes as compared with that for positive cluster ions. This phenomenon was most distinct at Utö (Fig. 4). The different mean sizes of cluster ion modes among the sites are indicative of different air chemistries (Eisele 1989a, 1989b, Eisele and Tanner 1990). The differences in negative and positive cluster ions and their mean sizes could, in principle, be used to analyse air chemistry when more laboratory measurements on various compounds will be available. The overall shape of the ion size distributions changed clearly with the changing ion sink. With an increasing ion sink, the cluster ion mode got smaller and the proportion of larger ions increased (Fig. 4).

The ion production rate and ion sink were calculated according to Hõrrak *et al.* (2005) for

Table 1. Mean values (± SD) of particle number concentrations and ion concentrations in different size classes during the measuring period at Utö, Hyytiälä and Tahkuse. All values are given in cm^{-3}.

	Utö	Hyytiälä	Tahkuse
Total particle concentration*	4800 ± 2400	3700 ± 3400	9900 ± 7100
Cluster ions (+) (< 1.6 nm)	250 ± 110	840 ± 250	390 ± 120
Cluster ions (–) (< 1.6 nm)	280 ± 120	770 ± 260	280 ± 120
Intermediate ions (+) (1.6–7 nm)	6 ± 14	13 ± 32	110 ± 130
Intermediate ions (–) (1.6–7 nm)	10 ± 24	21 ± 63	93 ± 150
Light large ions (+) (7–22 nm)	62 ± 74	74 ± 140	390 ± 380
Light large ions (–) (7–22 nm)	53 ± 76	73 ± 130	400 ± 380

* Note the slightly different size ranges measured between the three sites

the whole period and for all the three sites (Table 2). As one could expect the most continental site, Hyytiälä, had most of the time the highest ion production rates. The reason for higher ionization rate at Hyytiälä is the igneous bedrock (granites) ground, partly exposed or covered by only a thin layer of soil, which is known to have a considerably high content of radioactive matter (Laakso *et al*. 2004a, Hõrrak *et al*. 2005). On only few occasions, production rates at Utö or Tahkuse exceeded those at Hyytiälä. At Utö and Tahkuse, the ion production rates were on average quite similar, being 3.0 and 2.6 ion pairs cm^{-3} s^{-1}, respectively. Still, clear differences were observed during the measuring period. The average ion production rate at Hyytiälä was 6.4 ion pairs cm^{-3} s^{-1}, which is at about the same level as found earlier by Hõrrak *et al*. (2005).

Studies of ionizing radiation were previously done at the Hyytiälä site (Laakso *et al*. 2004a, Hirsikko *et al*. 2007). These studies separated ionization caused by radon decay and external radiation meaning cosmic radiation and gamma radiation from the ground. According to them radon produces on average about 10% of the ionization at Hyytiälä. The separation between cosmic and ground radiation could be estimated by using the nearly constant value for ion production by cosmic rays, 1.8 ion pair cm^{-3} s^{-1} (Hensen and Van Der Hage 1994, Carslaw *et al*. 2002, Belov *et al*. 2006, Kazil *et al*. 2006, Tinsley and Zhou 2006). As the average ion production rate at Hyytiälä was 6.4 ion pair cm^{-3} s^{-1}, the cosmic rays contributed, on average, about 30% to the total ion production rate at Hyytiälä during our measurement period. At Utö and Tahkuse, the contribution of cosmic rays to the ion production rate was estimated to be on average about 60%–70%.

The electrical state of aerosol particles in the nanometre size range in the natural atmosphere is not well known. Simultaneous measurements of aerosol particle size distributions and air ion mobility distributions enabled us to estimate the charging probabilities of atmospheric aerosol particles. This parameter can be obtained as the slope of the linear regression line on the scatter plot of the measured concentrations of total and charged particles for the same diameter interval (Vana *et al*. 2006). In this study we could com-

Table 2. Mean values (± SD) of ion production rate and ion sink during the measuring period at Utö, Hyytiälä and Tahkuse. Nucleation event days are indicated as follows: * = clear event, × = some indication of an event.

	Ion production rate (ion pairs cm^{-3} s^{-1})			Ion sink (10^{-2} s^{-1})		
	Utö	Hyytiälä	Tahkuse	Utö	Hyytiälä	Tahkuse
19 April 2004	7.1 ± 3.0	7.8 ± 3.4	2.9 ± 1.3	2.2 ± 0.3	1.6 ± 0.6	2.1 ± 0.4
20 April 2004	5.4 ± 1.7	9.4 ± 5.4×	3.5 ± 1.1	1.9 ± 0.4	1.9 ± 1.2×	1.9 ± 0.5
21 April 2004	4.1 ± 1.4	8.3 ± 4.2	4.1 ± 1.7	1.5 ± 0.4	1.2 ± 0.4	1.4 ± 0.3
22 April 2004	2.7 ± 1.0×	5.1 ± 1.6*	2.1 ± 0.8	0.6 ± 0.2×	0.7 ± 0.5*	0.8 ± 0.4
23 April 2004	3.0 ± 0.9	6.8 ± 2.5*	3.1 ± 0.7*	0.7 ± 0.1	1.3 ± 0.8*	1.8 ± 0.4*
24 April 2004	4.0 ± 2.0*	7.0 ± 2.3*	2.8 ± 1.3	1.0 ± 0.4*	1.0 ± 0.4*	1.5 ± 0.5
25 April 2004	4.3 ± 1.3*	7.0 ± 2.6*	3.0 ± 1.4	1.4 ± 0.3*	1.0 ± 0.4*	1.5 ± 0.4
26 April 2004	3.7 ± 1.2	7.8 ± 2.6*	3.5 ± 1.9*	1.3 ± 0.4	1.0 ± 0.4*	1.5 ± 0.4*
13 May 2004	1.9 ± 0.8*	5.7 ± 1.8*	2.1 ± 1.0×	0.5 ± 0.2*	0.5 ± 0.3*	0.6 ± 0.3×
14 May 2004	2.0 ± 0.7	6.4 ± 1.9×	2.7 ± 0.8×	0.5 ± 0.2	0.5 ± 0.2×	0.6 ± 0.1×
15 May 2004	2.3 ± 0.8	4.7 ± 1.2	2.3 ± 0.7	0.5 ± 0.1	0.5 ± 0.3	0.7 ± 0.2
16 May 2004	1.9 ± 0.8	5.5 ± 1.6×	2.1 ± 1.0*	0.4 ± 0.1	0.3 ± 0.1×	0.5 ± 0.3*
17 May 2004	2.2 ± 1.5×	6.6 ± 2.3*	2.4 ± 0.9*	0.5 ± 0.2×	0.6 ± 0.3*	0.7 ± 0.2*
18 May 2004	1.7 ± 0.8×	4.6 ± 1.1	2.9 ± 0.9×	0.6 ± 0.4×	0.6 ± 0.3	0.7 ± 0.3×
19 May 2004	1.9 ± 0.6×	5.7 ± 1.4*	2.4 ± 1.8	0.6 ± 0.2×	0.5 ± 0.2*	0.7 ± 0.2
20 May 2004	1.2 ± 0.5*	4.7 ± 1.3*	1.4 ± 0.5*	0.3 ± 0.2*	0.3 ± 0.1*	0.4 ± 0.1*
21 May 2004	1.1 ± 0.4*	5.0 ± 0.9*	1.7 ± 0.9*	0.3 ± 0.1*	0.3 ± 0.1*	0.4 ± 0.1*
Average	3.0 ± 1.6	6.4 ± 1.4	2.6 ± 0.7	0.9 ± 0.6	0.8 ± 0.5	1.0 ± 0.6

pare charged fractions of aerosol particles as a function of their size from the simultaneous measurements at three sites (Fig. 5). The size distributions of calculated charging probabilities were compared with the steady-state charge distribution obtained from Reischl *et al.* (1996). We can see that calculated charging probabilities, at least in the diameter range below 8 nm, were close to the steady state at all the three sites. In the size range below 5 nm, charging probabilities larger than the steady-state charging probability could indicate the presence of ion-induced nucleation, which was not observed here. Many studies of new particle formation (e.g. Kulmala *et al.* 2001a) outlined that the nucleation rate (or the formation rate of 1 nm particles) should be in the range of 10–100 cm^{-3} s^{-1} to explain the formation rate of 3 nm particles of about 1 cm^{-3} s^{-1}. The production of new particles by ion-induced nucleation is limited by the ionisation rate, which is about 6 ion pair cm^{-3} s^{-1} at Hyytiälä and about 3 ion pair cm^{-3} s^{-1} at Utö and Tahkuse. If we assume the estimates above to be correct, then the ionisation rate should be in the range of 10–100 cm^{-3} s^{-1} to explain the results.

No significant diurnal variation was seen in the total particle number concentration at the Utö station. A weak diurnal variation was observed at Hyytiälä and a clear diurnal variation at Tahkuse. At both sites the average concentrations peaked between 10:00 and 14:00, probably due to new-particle formation taking place in that time frame on a few days. In total ion concentrations (diameter < 40 nm) no significant diurnal variation was observed at any of the sites. At Hyytiälä and Tahkuse, cluster ion concentrations (diameter < 1.6 nm) showed a diurnal variation that was inversely related to that of particle concentrations. This feature can also be related to the ion sink provided by aerosol particles. At Utö cluster ion concentrations showed no significant diurnal variation. The lack of diurnal variation at Utö might be due to smaller variation in meteorological parameters (i.e. temperature and wind speed) in the marine environment, since their variation has been observed to have an influence on ion concentrations (Hõrrak *et al.* 2003). At all sites and size ranges, the diurnal variation of negative and positive ions showed a similar behaviour.

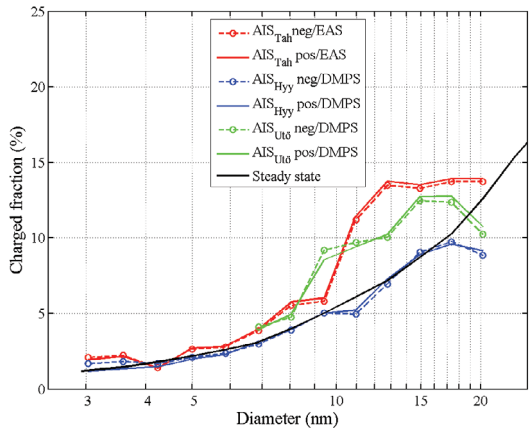

Fig. 5. Charged fraction as a function of particle diameter from 19 April to 21 May 2004 in the three locations.

Case 1: air masses with minor continental influence

In order to provide some insight into the changes in air ion size distributions, we consider a couple of example days in more detail. First we present a day with air having a marine origin (18 May 2004; Fig. 6). On this day, the air masses were arriving almost directly from the west from the Atlantic Ocean and had passed southern Scandinavia prior to their arrival at the measuring sites.

The highest particle number concentration in the size range 7–500 nm was measured at Tahkuse, being on average 6000 cm^{-3}. Utö and Hyytiälä had clearly lower concentrations of 3700 cm^{-3} and 2500 cm^{-3}, respectively. Particle number size distributions had relatively similar shapes at all the sites with a strong mode that peaked at about 40–60 nm diameter. At Tahkuse the distribution was a bit broader than at Utö and Hyytiälä, and it extended to smaller sizes. The broader size distributions observed at Tahkuse might be partly due to instrumental differences, since the EAS at Tahkuse has a lower size resolution than the other two instruments. Also the fact that the EAS does not measure the dry size, as the DMPS does, may broaden the Tahkuse distribution slightly but only to larger sizes.

Total air ion concentrations (0.35–40 nm) were largest at Tahkuse and the corresponding ion size distribution was dominated by large ions in roughly a 20–40 nm range. Above 20 nm, the

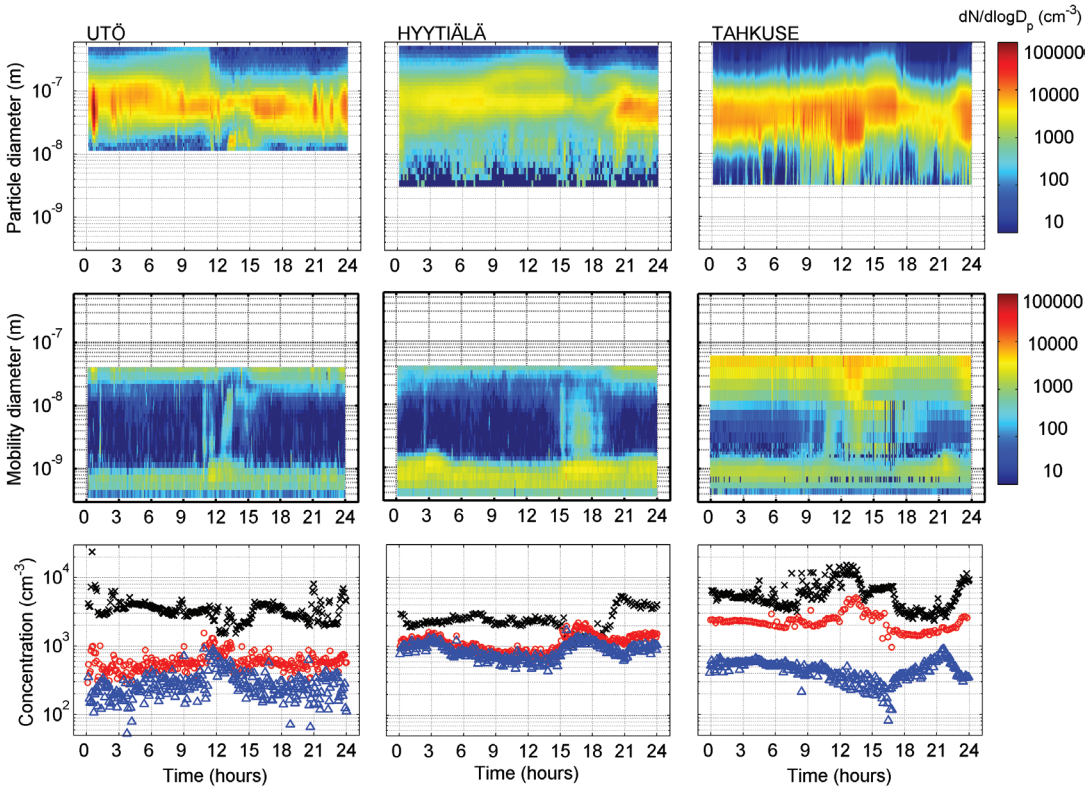

Fig. 6. One-day data of particle number size distributions (upper row) and negative ion size distributions (middle row). The lowest row includes particle concentration (black crosses), negative ion (< 40 nm) concentration (red circles) and cluster ion (< 1.6 nm) concentration (blue triangles) in the three sites (from left to right: Utö, Hyytiälä and Tahkuse) on 18 May 2004.

dominant ion source is the coagulation of cluster ions with pre-existing aerosol particles. The shape and size of this large ion mode followed quite well the corresponding aerosol particle mode measured by the EAS in Tahkuse, giving indications that this ion mode originated from the coagulation of cluster ions with aerosol particles. Utö had the lowest concentration of ions (0.35–40 nm), probably due to a lower source for ions as compared with the other two more continentally-located stations. The average ion production rates for this day were 4.6, 2.9 and 1.7 ion pairs cm^{-3} s^{-1} at Hyytiälä, Tahkuse and Utö, respectively. On this day, ion sinks were at about the same level at all the sites, being $0.6–0.7 \times 10^{-2}$ s^{-1}.

Ion cluster concentrations are clearly the result of the competition between ion sources and sinks. Ions are formed by the radioactive decay of radon over land and by cosmic ray ionization, as well as by ionizing radiation from the ground. The Utö island with a minimum land area around it had the lowest cluster ion concentrations. Hyytiälä in mainland Finland had the highest cluster ion concentration and Tahkuse close to the Baltic Sea had a concentration in between the two other sites. The mean diameters of negative and positive ion clusters were in the range of 0.6–0.8 nm and 0.8–0.9 nm, respectively, at all the sites. We may clearly see that cluster ions (< 1.6 nm) dominated total ion concentrations (< 40 nm) at Hyytiälä and Utö, whereas larger ions (20–40 nm) were dominating at Tahkuse (Fig. 6).

Case 2: air masses with major continental influence

The second case (20 April 2004; Fig. 7) presents a day with air masses coming from the south-eastern direction and having strong continental

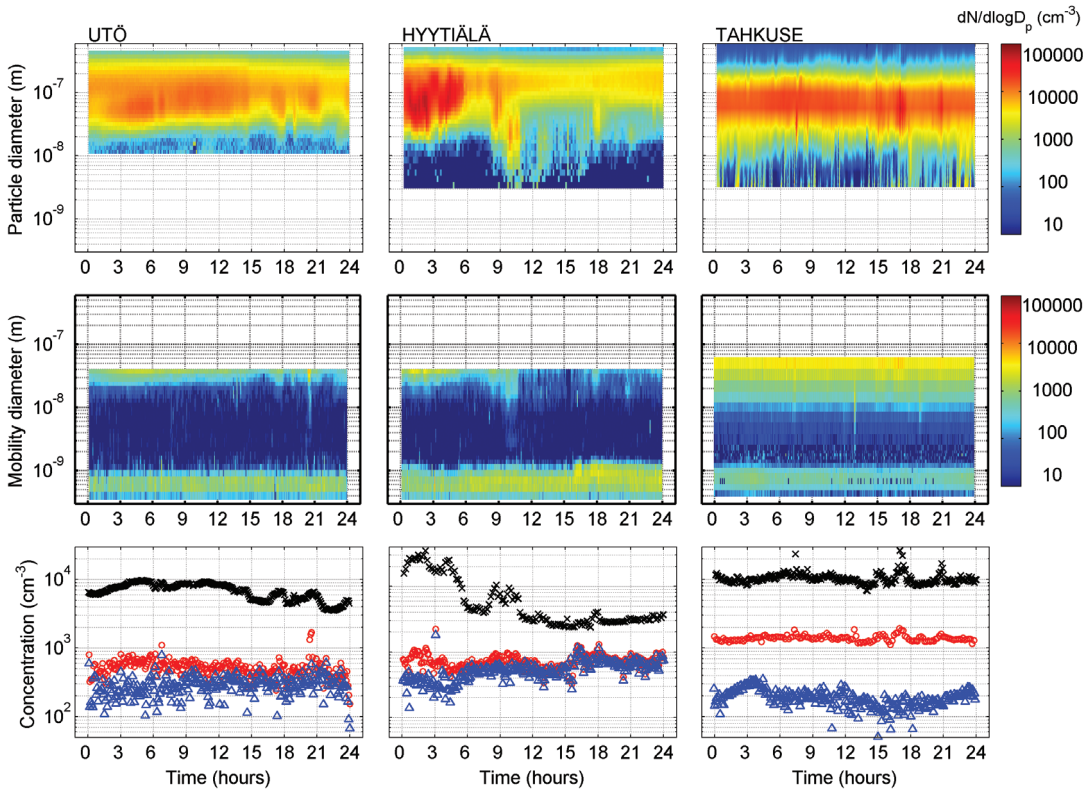

Fig. 7. Same as Fig. 6 except on 20 April 2004.

histories. All the stations had higher particles concentrations than in Case 1. Tahkuse again showed the highest particle number concentrations, the average being 10 400 cm^{-3}. The Utö and Hyytiälä sites had also relatively high daily-average particle number concentrations of 6800 cm^{-3} and 7800 cm^{-3}, respectively. Particle number size distributions peaked in the diameter range 70–90 nm, which are substantially larger values than in Case 1. The shapes of the particle number size distributions were very similar at Utö and Hyytiälä. As compared with these two sites, Tahkuse had typically bit broader particle number size distributions that peaked at smaller sizes. One reason for this feature might be the longer time the particles had for growth before reaching Utö and Hyytiälä, since the air mass was arriving from the direction of Tahkuse.

Total ion concentrations (0.35–40 nm) were largest at Tahkuse due the high number concentration of large ions. As compared with Case 1, ion concentrations and especially the concentrations of cluster ions were significantly lower due to the three times larger sink caused by pre-existing aerosol particles. The average ion sink on this day was 1.9×10^{-2} s^{-1} at all the sites. The effect of the increased ion sink was best visible at Hyytiälä with the highest ion source of these three locations. At Utö the change in ion concentration was not so large. The daily-average ion production rate at Hyytiälä was 9.4 ion pairs cm^{-3} s^{-1}. At Utö and Tahkuse, these values were 5.4 and 3.5 ion pairs cm^{-3} s^{-1}, respectively. At Hyytiälä one can see an increase in the cluster ion concentration when the particle concentration (i.e. sink) decreased. In this continental case, cluster ion concentrations were closer to each other than in Case 1 at all the sites, probably due the higher and similar ion sinks. At all the sites, the mean diameters of negative and positive ion clusters were in the range 0.5–0.7 nm and 0.8–1.0 nm, respectively.

Nucleation events

New particle formation and indications of cluster

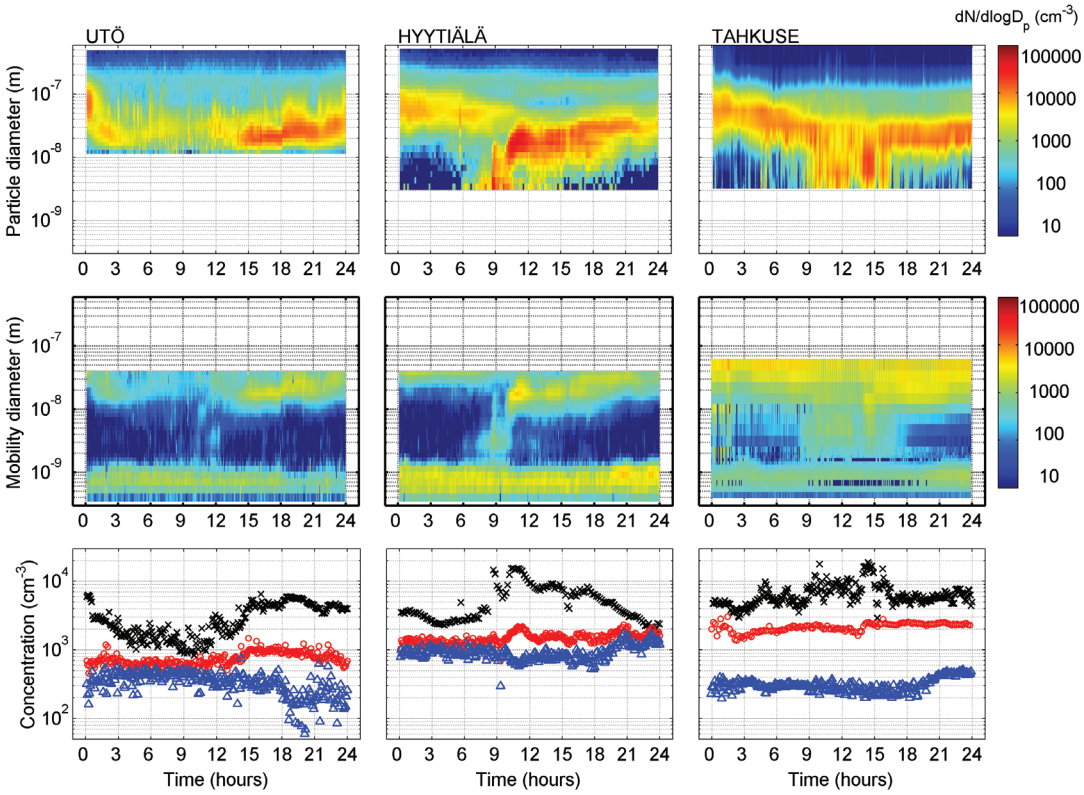

Fig. 8. Same as Fig. 6 except on 20 May 2004.

ions growing to larger sizes were observed at all the sites. During the measurement period when we had data from all the sites (17 days), clear new-particle formation was observed during 11 days at least at one of the sites. On four days, these events took simultaneously place at all the three sites. To provide some insight also into the new particle formation and ion bursts, next we consider two example days in more detail.

The charged fractions of particles according to their sizes were calculated for six individual event days for all the sites, including the two example days considered below. The results showed that ion-induced nucleation may have played some role on one of the six days (Case 3, 20 May 2004). On the other days ion-induced nucleation was not significant. One interesting finding was that during four of the six days, the negative charged fraction (in size range 3–5 nm) at Hyytiälä was significantly higher than the positive one. At the same time at Tahkuse both positive and negative charged fractions were close to each other.

Case 3: air masses with minor continental influence

First we present a day with air masses having a marine origin (20 May 2004; Fig. 8). These clean air masses originated from the North Atlantic or Arctic Ocean and had a cross over Scandinavia before reaching the measuring sites. This is the common air mass pattern when new particle formation events are being observed over Scandinavia (Kulmala *et al*. 2001b, Komppula *et al*. 2003a, 2003b, Tunved *et al*. 2003, Dal Maso *et al*. 2007).

On this day, some new particle formation was observed at all the sites. Pre-existing particle concentrations were at about the same level at Utö and Hyytiälä (~2000 cm^{-3}) and slightly higher at Tahkuse (~5000 cm^{-3}).

Total ion concentrations (0.35–40 nm) were at about the same level as in Case 1. Some activity in ions growing from the cluster size to larger sizes was observed at all the sites. The difference in ion sources (and sinks) could be observed very

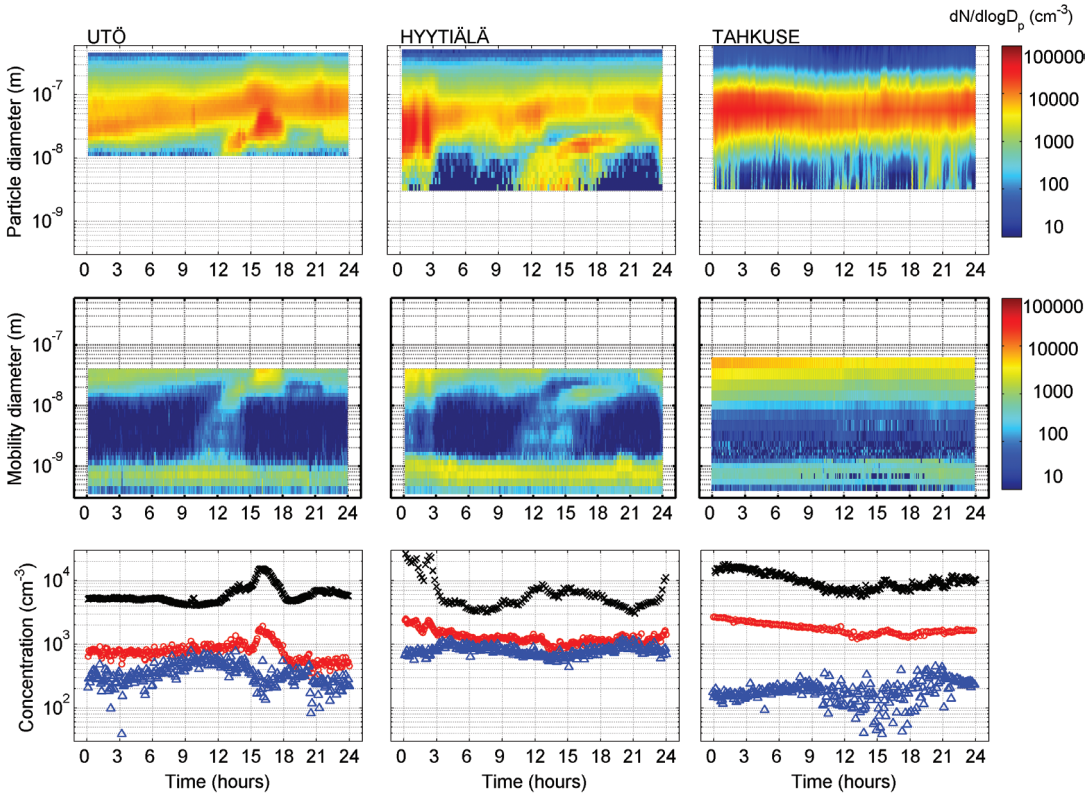

Fig. 9. Same as Fig. 6 except on 24 April 2004.

well. Utö, having the lowest particle concentration before the event and therefore the lowest ion sink, had still the lowest ion concentrations. This is a clear indication of a lower source rate of ions at Utö. The calculated ion production rate at Utö was 1.2 ion pairs cm^{-3} s^{-1}, while at Hyytiälä and Tahkuse these values were 4.7 and 1.4 ion pairs cm^{-3} s^{-1}, respectively.

Case 4: air masses with major continental influence

Case 4 (24 April 2004; Fig. 9) presents a day with slightly different air mass history than Case 3. Now the air masses originated from the Arctic Ocean but approached the sites from the east over Russia, having a more continental influence.

On this more polluted day, no particle formation was observed at Tahkuse and only weak formation was observed at Utö and Hyytiälä. Pre-existing particle number concentrations were clearly higher than in Case 3 at all the sites. On this day, the ion sink was 1.5×10^{-2} s^{-1} at Tahkuse and 1.0×10^{-2} s^{-1} at Utö and Hyytiälä on average. The background Aitken mode size distributions were close to each other at all the sites. The shape of the size distribution was somewhere between the marine and continental cases (Cases 1 and 2), having one distinct mode peaking at 40–70 nm. At Utö and Hyytiälä, also a clear growth of the pre-existing Aitken mode was seen.

At Utö and Hyytiälä, some activity of ions growing from the cluster sizes to larger sizes was observed also in this case. The ion production rate at Hyytiälä was 7.0 ion pairs cm^{-3} s^{-1}. At Utö and Tahkuse these values were 4.0 and 2.8 ion pairs cm^{-3} s^{-1}, respectively. Overall it seems that more polluted continental air masses had higher ion production rates as compared with those of air masses with a minor continental influence (Cases 1 and 3). The higher ion sink at Tahkuse lowered the cluster ion concentrations to the

same level as at Utö or even a bit lower. The ion concentrations (0.35–40 nm) at Tahkuse were again dominated by large ions.

Conclusions

The measurements at the three sites gave us an opportunity to investigate the variability of the ion concentrations in the Baltic Sea region. Having one site on an island in the Baltic Sea and two other sites at more continental locations, but still not far away from the coast of the Baltic Sea, provided an interesting basis for the study. More insight into the dynamics of the air ion population was obtained by using simultaneous particle number size distribution measurements in all the three sites.

The behaviour of cluster ion (diameter < 1.6 nm) concentrations revealed clearly the competition between ion sources and sinks. Ions are formed by ionizing radiation from the ground, by the radioactive decay of radon over land, and by cosmic ray ionization. It was estimated that during the measurement period the cosmic rays contributed, on average, about 30% to the total ion production rate at Hyytiälä and about 60%–70% at Utö and Tahkuse. The Utö island with a minimum land area around it had the lowest cluster ion concentrations. Hyytiälä in the mainland Finland had the highest cluster ion concentrations probably due to the granite soil as a source of radon, whereas the Tahkuse station close to Baltic Sea had cluster ion concentration values mostly between those for the two other sites. Cluster ion concentrations were observed to be about three times smaller at Utö as compared with those at Hyytiälä. The lower cluster ion concentrations over the Baltic Sea may be due to lower ionization rate in the cleaner marine environment and also due to higher wind speeds than over the continent. The other mainland site, Tahkuse in Estonia, showed also lower cluster ion concentrations than Hyytiälä, probably due to higher total aerosol concentration levels and thus higher ion sinks, and probably also due to lower radon concentrations. In the continental air mass case, the cluster ion concentrations were low and close to each other at all sites, probably due the higher sink caused by particles.

Mean concentrations of intermediate ions in the diameter interval of 1.6–7 nm were generally low varying from 6 cm^{-3} at Utö to 110 cm^{-3} at Tahkuse, but reached several hundreds or occasionally more than 1000 cm^{-3} during nucleation episodes in all the three locations. Mean values of total particle number concentration during the measuring period were 9900 cm^{-3} at Tahkuse, 4800 cm^{-3} at Utö and 3700 cm^{-3} at Hyytiälä.

The charged fractions of aerosol particles as a function of their size were calculated. The charging probabilities, at least in diameter range below 8 nm, were observed to be close to the steady state at all the three sites. Only one case showed some indication of ion-induced nucleation. This suggests that, at least in this time period, ion-induced nucleation was not playing a major role.

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