

**Atmospheric trace  
gas measurements  
using IMS**

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# Atmospheric trace gas measurements using ion mobility spectrometer

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## Abstract

Ion mobility spectrometer (IMS) was implemented to measure gas phase compounds from ambient air in order to study the suitability of the technique for on-line atmospheric measurements. The measurements took place at the SMEAR II station in Hyytiälä, Finland during spring periods on 2008 and 2009. We were able to separate several different atmosphere related ion mobility peaks from the measured ion mobility distributions. The hypothetic origins of these peaks are discussed accompanying the comparison with earlier trace gas measurements by different techniques. The potential of the IMS for atmospheric studies utilizing the concept used here was found out to be in monitoring the overall cleanness of prevailing atmospheric conditions as well as fast detection of the changes of those conditions. With further developing of the technique based on experience gathered in this study the IMS could be tuned to better respond to current measurement needs in atmospheric studies.

## 1 Introduction

In atmosphere number of different trace gases are continuously present (e.g. Seinfeld and Pandis, 2006). Some of these trace gases have been postulated to participate on the formation and growth of atmospheric particles (e.g. Bzdek and Johnston, 2010). According to current knowledge, the most important trace gases in the point of view of the formation and growth of the atmospheric particles are sulphuric acid (e.g. Kulmala et al., 2000), amine compounds (e.g. Smith et al., 2010; Mäkelä et al., 2001) and different oxidation products of monoterpenes (e.g. Laaksonen et al., 2008). To be able to study the role of different trace gases to new particle formation and growth as well as to model those phenomena, continuous and accurate measurements of different trace gases are required. With current measurement techniques used in atmospheric sciences, all of the trace gases present in the atmosphere cannot be measured. Thus new techniques and measurement procedures are needed.

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Several different measurement techniques are being used for atmospheric trace gas measurements. A recent review of these techniques can be found from Farmer and Jimenez (2010). For trace gas measurements, techniques utilizing mass spectroscopy are widely used these days. Especially chemical ionization mass spectrometry (CIMS) has gained popularity (Sellegrì et al., 2005; Huey, 2007). CIMS successfully used for detection of biogenic volatile organic compounds as well as amine compounds is known as PTR-MS, referring to proton transfer reactions as an ionization method. PTR-MS has been used with success also for on-line atmospheric measurements (e.g. de Gouw and Warneke, 2007; Eerdekens et al., 2009; Rinne et al., 2005). The artificial ionization, used in most measurement techniques, may have influence on measurement results due to fragmentation. One quite recently introduced method, also based on mass identification, is APi-TOF. With this technique atmospheric natural charged ions can be measured directly from atmosphere without artificial ionization (Junninen et al., 2010). The main disadvantage of measurement techniques based on mass identification can be considered to be the need of vacuum, while the vacuum e.g. adds up the requirements for maintenance and complicates continuous sampling in field conditions. In lack of an ideal measurement technique for atmospheric trace gas measurements, different approaches are needed for different purposes as well as to complement each other.

One measurement technique not yet fully utilized for direct atmospheric measurements is the ion mobility spectrometry (IMS). The technique is very sensitive for trace gas concentrations for a number of different compounds, starting from the low ppb-levels (e.g. Eiceman and Karpas, 2005; Baumbach and Eiceman, 1999). Thus it can be considered as a potential technique for atmospheric studies. Ion mobility spectrometer is a measurement technique, which is based on electrical mobility of ions. The IMS operates in atmospheric pressure thus the disadvantages of a vacuum are avoided. Nevertheless, also in IMS-technique the sample gas is artificially ionized but as well as in PTR-MS the ionization takes place within the carrier gas and it is thus considered as a soft ionization mechanism. Basically, IMS technique produces a mobility

distribution formed by artificially ionized gas phase compounds present in the sample gas, and the identification of different compounds can be made e.g. based on reference measurements of known compounds (Eiceman and Karpas, 2005).

IMS is widely used in the research field of security and protection (Eiceman and Karpas, 2005), but the technique has been utilized also for e.g. medical sciences (e.g. Baumbach and Westhoff, 2006) and analytical chemistry (e.g. Pedersen et al., 2008). For atmospheric related research IMS has been used earlier in laboratory for nucleation studies (Nagato et al., 2005; Viitanen et al., 2010) and for studying the ion evolution of ambient air (Nagato and Ogawa, 1998). In the field IMS has been used for measuring atmospheric ammonia (Myles et al., 2006; von Bobruzki et al., 2010). In this study the ion mobility spectrometer (IMS) is implemented for direct atmospheric sampling on site in order to find out the potential of this technique for current measurement requirements in atmospheric studies.

## 2 Experimental

### 2.1 Measurement site and time

The measurements took place in SMEAR II station in Hyytiälä, Finland. The station is situated in the boreal forest without major pollution sources nearby. The background air is relatively clean thus the direct sampling with the IMS was considered possible. More detailed description of the station can be found from (Hari and Kulmala, 2005). For IMS data-analysis a spring period from the years 2008 and 2009 was chosen, while the spring time represents a most active period in particle formation (Mäkelä et al., 2000) and is also the time for the spring recovery of vegetation, which has been postulated to be connected to particle formation (DalMaso et al., 2009).

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## 2.2 Ion mobility spectrometry

Two commercial ion mobility spectrometers (RAID I, Bruker Daltonics GmbH) were used, and they are indicated here as IMS1 and IMS2. The two devices used were identical, with only minor differences in dimensions and operating hours. The operation principle of the IMS based on time-of-flight method is illustrated in Fig. 1. Basically the IMS consists of ionization region, drift region and collector. RAID I uses a radioactive source  $^{63}\text{Ni}$  (activity 15 mCi/555 MBq) for ionization. The grid between ionization and drift regions is set to guide a sample pulse with width of 0.3 ms into the drift region. The sample ions drift to the collector plate due to a constant electric field of  $252 \text{ V}(\text{cm})^{-1}$  (IMS1) and  $254 \text{ V}(\text{cm})^{-1}$  (IMS2), and the arriving time and the current caused by the ions are recorded. The resulted time-of-flight distribution is converted to reduced mobility according to Eq. (1).

$$K_0 = \frac{l_{\text{eff}} T_0 \rho}{E t T \rho_0} \quad (1)$$

where  $l_{\text{eff}}$  is the effective drift tube length,  $E$  is the electric field,  $t$  is the drift time of an ion,  $T_0$  and  $\rho_0$  are the temperature and pressure in normal conditions,  $T$  and  $\rho$  are the temperature and pressure of the drift tube.

For IMS1 effective drift tube length value of 5.840 cm was used, which was confirmed by using 2,6-di-tert-butyl pyridine (Viitanen et al., 2008). For IMS2 the effective drift tube length has been determined to be 5.764 cm (Viitanen et al., 2008). The RAID I aspirated automatically the sample air with the volume flow rate of  $0.4 \text{ l min}^{-1}$ . From this sample flow a drift flow is separated. The sample flow is guided to the ionization region and forwarded to the drift region while the drift flow is filtered and introduced to the drift region opposite to sample flow (see Fig. 1). The operation hours of the filters used for drift gas purification are expected to influence on the composition of the drift gas in time when measuring long term continuous periods. Contaminated drift gas can change the reduced mobility values measured (Fernández-Maeatre et al., 2010). This fact may also be one explanation for possible differences between different devices in

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field conditions. Thus, the filters need to be dried or changed regularly. In general, the IMS technique allows also the use of the external drift gas, e.g. purified and dried instrument air from the gas cylinder. With this kind of concept the issues related to the aging of the filters discussed above would be naturally avoided but at the same time the suitability as a field device would suffer.

The membrane which is typically used in ion mobility spectrometers for sample gas flow pre separation, was removed from both of the devices to allow direct sampling of the atmospheric trace gases. The IMS measurement setup without the membrane may complicate the measured ion mobility distribution and lower the sensitivity, while water vapour, ammonia and other typically unwanted compounds in analytical studies are here allowed to interfere the measurements (Eiceman and Karpas, 2005). By this concept we wanted to measure the atmospheric air as it is. This way all the measured ion mobility peaks will be most likely formed as a combination of trace gas molecules, water vapour and some ligands.

During the field measurements, the IMS device was situated indoors inside a cabin, where the room air temperature was kept constant by air-conditioning. While we did not want to change the prevailing gas composition of the sample air, external heating of the devices was not used resulting the operation temperature of the devices to remain at approximately 30 °C. As an inlet line, 6 mm Teflon tube was used. The inlet line (app. 2 m long) was situated app. 1 m above ground level and faced down so that there was no rain drop or snowfall access into the tube. Both positive and negative polarity was sampled in every other minute. One measurement period lasted typically app. 3 days, after which a new period was manually started so that the break between the measurement sets was no more than few minutes. During the whole measurement period a few power failures and maintenance breaks occurred.

### 2.3 Data processing

Examples of positive and negative ion distributions measured from ambient air are presented in Fig. 2. The measured data was averaged over 10 min. From the measured

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IMS distribution six different positive peaks and five different negative peaks could be generally distinguished. Each peak was searched from the whole measurement period using a peak identification procedure of Matlab (O'Haver, 2006). The changing humidity conditions during the measurements can lead to shifting of the peaks along the mobility scale as was shown by Mäkinen et al. (2011). This was compensated by using manually fixed boundaries for reduced mobility values shown in Fig. 2. The code recorded the height and full width at half maximum of each peak in respect to time. When the height is multiplied by the width at half maximum a current signal of each peak is obtained. The elevating humidity can lower the sensitivity (Mäkinen et al., 2011). Since the humidity conditions usually vary during the measurements, some inaccuracies may be induced to the recorded peak heights.

In IMS technique utilizing a radioactive source the amount of the charge available for different molecules to be ionized, is constant. The ionization mechanism of the trace compounds is based on proton transfer reaction between the reaction ion and the trace gas molecule. In this case, the positive reaction ions are mainly protonated water molecules  $O^+(H_2O)_n$  (Eiceman and Karpas, 2005). The proton affinity of water is  $691 \text{ kJ}(\text{mol})^{-1}$  (Haynes, 2011) thus compounds with higher proton affinity are likely to be observed in the IMS distribution. On negative polarity the reaction ions are most likely formed mainly by  $O_2^-(H_2O)_n$  (Eiceman and Karpas, 2005). This leads to the fact that, while the decreasing trend of the reaction ions indicates that there are trace gas compounds present in the measured sample, the fraction of reaction ions in the ion mobility distribution is a measure of the purity of the measured sample. Based on this, the electric current from each peak was normalized by dividing the current from the peak by the current of the reaction ions. After this procedure, five positive and four negative ion mobility peaks were traced for further analysis. Thus these peaks were chosen for analysis here and considered as atmosphere related ion mobility peaks.

The selected “atmosphere related ion mobility peaks” to be traced in this study, are listed in Table 1. Despite the reduction of the mobility values some fluctuation of the peak values still occurs. In Table 1 the maximum and minimum value for each peak

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over the whole measurement period is given. From this, a midpoint is calculated and given as a mean reduced mobility value for each peak. Using the computational value for mean peak mobility, the corresponding approximate mass was calculated using a fit based on Kilpatrick's old data (Mäkelä et al., 1996) and given within computational accuracy of 20 % (Griffin et al., 1973).

Based on current knowledge on the atmospheric relevant trace gases and literature values on reduced mobilities and masses, conservative estimates about the origin of these peaks can be given. The compound that is assumed to form the ion mobility peak in question most likely includes also water and other ligands which have an effect on the mobility and further on the calculated mass.

On positive polarity the ion mobility peak with highest mobility, marked here as  $A+NH_3$ , corresponds most likely the peak formed by ammonia and amines, mainly dimethylamine (DMA) and trimethylamine (TMA). All of these compounds are present in the atmosphere at trace concentrations (Seinfeld and Pandis, 2006; Ge et al., 2011). The proton affinity of ammonia and di- and trimethyl amine are comparably high,  $854 \text{ kJ}(\text{mol})^{-1}$ ,  $930 \text{ kJ}(\text{mol})^{-1}$  and  $949 \text{ kJ}(\text{mol})^{-1}$ , respectively (Haynes, 2011). The reduced mobility values found in literature also support the hypothesis (Karpas, 1989; Mäkinen et al., 2011).

The positive peak with reduced mobility around  $2.11 \text{ cm}^2(\text{Vs})^{-1}$  was the most intensive one. This indicates that it is formed by reaction ions (RIP), i.e. mainly water clusters (Eiceman and Karpas, 2005). The positive peak P1 has a reduced mobility value close to acetone (Eiceman and Karpas, 2005; Rudnicka et al., 2010), which is also present in atmosphere with trace concentrations (e.g. Eerdekens et al., 2009) and has a proton affinity over  $800 \text{ kJ}(\text{mol})^{-1}$  (Haynes, 2011). The acetone concentration in Hyytiälä site has been reported to be roughly around 1 ppb (Eerdekens et al., 2009). The positive peak P2 can be considered to be close to reduced mobility recorded for supposed oxidation product of  $\alpha$ -pinene in environmental chamber studies (Viitanen et al., 2010). The positive peaks P3 and P4 represent already larger and heavier ionic species indicating large molecules, dimers of some compounds or heterodimers of two

different compounds.

On positive polarity, there are also other possible candidates; e.g. acetaldehyde and formaldehyde have been measured in Hyytiälä (Hellén et al., 2004; Eerdekens et al., 2009). The literature values of reduced mobility for these compounds are 2.02 cm<sup>2</sup>(Vs)<sup>-1</sup> and 2.12 cm<sup>2</sup>(Vs)<sup>-1</sup>, respectively (Eiceman and Karpas, 2005), thus they cannot easily be separated from the reaction ion peak with the measurement setup used in this study. At Hyytiälä site also isoprene (PA 826.4 kJ(mol)<sup>-1</sup>, Haynes, 2011) has been measured with concentration of about 100–200 ppt including some other interfering compound (Sellegri et al., 2005). There is some variation in the reduced mobility values for isoprene found from the literature. Eiceman and Karpas (2005) reported three peaks with reduced mobility values of 1.99, 1.73 and app. 1.45 cm<sup>2</sup>(Vs)<sup>-1</sup> and Rudnicka et al. (2010) reported two, 1.65 cm<sup>2</sup>(Vs)<sup>-1</sup> and 1.53 cm<sup>2</sup>(Vs)<sup>-1</sup>. Nevertheless, the atmospheric concentration of isoprene is relatively low, thus, most likely it is not detected with the IMS-instrument used here.

The negative peaks PN0 and PN00 were measured quite rarely and only during the measurement period on 2009. The negative reaction ions (RIN) are believed to form the peak with reduced mobility  $-2.39 \text{ cm}^2(\text{Vs})^{-1}$  while it is the most intensive peak throughout almost the whole measurement period. Just next to RIN, the peak PN1 was present, leading to the fact that these two peaks cannot be completely separated from each other. Also occasionally PN1 was more intensive than RIN.

Unidentified negative ion mobility peaks are most likely small acids present in atmosphere but the lack of literature values for reduced ion mobilities of atmospheric compounds creates inaccuracy and an uncertainty for peak identification here. Trace concentrations of small acids e.g. Formic acid, Acetic acid and Propionic acid have been measured from atmosphere varying from tens of ppt to few ppb-range (Hofmann et al., 1997; Suzuki et al., 1997). Also natural ions measured from the atmosphere in this size range, such as HSO<sub>4</sub><sup>-</sup> have been reported (Ehn et al., 2010). Smith et al. (2010) used TDCIMS to analyse chemical composition of particles formed during the new particle formation event. They reported positive ions such as dimethylammonium,

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trimethylammonium and acetaldehyde, and negative ions such as formic acid,  $\text{NO}_3^-$ , propanoic acid, hydroxyacetic and  $\text{SO}_3^-$  found from particles. Acetic acid formed both positive and negative ions (Smith et al., 2010). These findings support our hypothesis especially on the origin of negative ion mobility peaks.

## 2.4 Measurement techniques used

The two individual IMS units were used mainly in turn: IMS1 was used during May 2008 and March-May 2009 and IMS2 was used during April 2008. A parallel measurement period for the two devices was conducted for three weeks in May 2008, for comparison (see Fig. 3). In Fig. 4a–e the intensities for atmospheric ion mobility peaks from both IMS-devices are shown. The  $\text{A}+\text{NH}_3$  – peak has quite the same intensity in both devices. For other peaks IMS2 is showing a lower intensity than IMS1. Figure 5a–b shows corresponding negative ion peak intensities. There is also a slight difference in the measured intensity of the peak PN1 between the devices, but in this case IMS2 measures slightly higher intensity than IMS1. IMS1 is detecting the peak PN2 more effectively than IMS2. The differences between the results gained by different IMS-devices are probably caused by the differences in drift gas filters as discussed in Experimental section. Beside the different composition of the drift gas caused by the filter ageing, the data processing method used for peak determination may be a reason for slight variation between the peak intensities presented here. Despite the differences in peak intensities the time behaviour of the peaks were comparable.

Simultaneously with IMS-measurements also other parameters were monitored at the site (Hari and Kulmala, 2005). The parameters and measurement height chosen for consideration here are wind direction and speed (8.4 m), UVA- and UVB- radiation (18 m), PA-radiation (74 m), precipitation, pressure, temperature and relative humidity (all at 4.2 m). The trace gas data used here are  $\text{NO}$ ,  $\text{NO}_x$ ,  $\text{O}_3$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{CO}$ , all measured at the height of 4.2 m. The submicron particle concentration and number size distribution were measured with differential mobility particle sizer (DMPS).

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For the data measured at the SMEAR II station 30 min averages was used. To be able to compare individual IMS peaks with different additional parameters, the linear interpolation was used and  $R^2$ -value was calculated for every compared pair.

### 3 Results and discussion

#### 3.1 Time series

From the measured data, several ion mobility peaks were separated. Time series along the measurement periods of these atmospheric ion mobility peaks have been plotted in Figs. 4–7.

##### 3.1.1 Positive ion mobility peak distributions

As an overall remark of the different peak intensities, it can be stated that the trace gas concentrations increased towards the summer. This is most likely caused by the change of the season with increasing temperature, vanishing snow cover and increasing vegetation activity. The increasing trace gas concentrations towards the end of May can be seen e.g. in the behaviour of the positive peak intensity of the peak P3. It was not detected at the beginning of the measurement period of 2009 but it appeared in the end of April and showed slightly increasing trend towards the end of the measurement period. The peak P4 was present only during one clear period at the very end of May 2009. Also the peak A+NH<sub>3</sub> showed increasing intensity trend towards the end of the measurement period 2009 (Fig. 6a). Clear trend along the measurement period of 2009 of the intensity of the peak P1 cannot be seen while only couple of concentration bursts were recorded (Fig. 6b). The peak P2, which is assumed to be related to the  $\alpha$ -pinene oxidation products, was measured throughout the measurement period of 2009 and showed also an increasing trend towards the end of May 2009 (Fig. 6c).

During the measurement period of 2008 the lack of data on March prevents the comparison of the peak intensities in the colder period of the spring, thus the increasing

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trend of the trace gas intensities along the spring is not that clearly seen as in 2009. The  $A+NH_3$  – peak did show neither a strong variation in intensities during the measurement period on 2008, nor a clear increase towards the summer during this period. In the case of the peak P1 the measurement result in 2008 corresponded the one measured in 2009 without clear change on intensity along the measurement period (Fig. 4b), but in 2008, this peak was detected more often than in 2009. The peak P2 was not showing a clear increase towards the end of May 2008. On 2008 the peaks P3 and P4 did not either have a clear monthly variation on April–May 2008 (Fig. 4d–e), but compared to the measurement results of 2009, these peaks were detected already at the beginning of April 2008. This might be due to either differences between atmospheric conditions in different years or differences in sensitivity of the IMS-devices.

### 3.1.2 Negative ion mobility peak distributions

Similar to positive ion distribution, also the trace gas intensities on negative polarity increased along the measurement periods when the spring season proceeded. The peak PN1 was detected only from the beginning of April 2009 and from the end of April 2008. The peak PN2 was detectable throughout the measurement period of 2009 showing relatively strong variation and increasing trend towards the end of May 2009. In 2008, PN2 was also detectable with slightly increasing intensity towards the end of the measurement period. Negative ion mobility peaks PN0 and PN00 were measured only during the measurement period in 2009. The peak PN00 started to show response at the end of the measurement period with strongest intensity at the very end of May 2009. The peak PN0 was measured only a few times during the whole measurement period of 2009.

From the measured data during spring months 2008 and 2009, a clear trend of increasing trace gas compositions towards summer can be seen. The monoterpene concentrations have been reported to be at the highest during the summer months (Hakola et al., 2009). Eerdekens et al. (2009) measured, among other VOCs, acetone during 18–30 April 2005 in Hyytiälä, where also acetone showed higher concentrations

during warmer than colder measurement period. Taipale et al. (2010) have shown that also the monoterpene emissions are at their highest in June.

### 3.2 Correlation studies

Several meteorological parameters, radiation parameters and additional trace gas concentrations were compared with the abundance of atmospheric related ion mobility peaks. No clear correlations were achieved between any peak and additional parameter through the whole dataset. The lack of clear correlation between atmosphere related ion mobility peaks and gas phase compounds (NO, NO<sub>x</sub>, O<sub>3</sub>, SO<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and CO) measured at Hyytiälä site indicates that, at least none of those ion mobility peaks are formed directly from the gas phase compounds in question. This also supports the estimation about the origin of the atmosphere related ion mobility peaks given in Experimental and Table 1. The fact that the ion mobility peaks did not correlate with meteorological parameters (UVA- and UVB- and PA-radiation, precipitation, pressure, temperature and relative humidity) indicates that the trace gases forming the atmosphere related ion mobility peaks are not, at least directly, dependent on one meteorological factor only, even though e.g. elevating temperature seems to have an indirect influence on some of the peaks as was shown above. The correlation between atmosphere related ion mobility peaks with wind speed and wind direction was studied as well. In these cases, the poor correlations support the interpretation that the trace gases generating the atmosphere related ion mobility peaks were forming mainly locally.

### 3.3 Temporal behaviour

In order to find out the temporal behaviour of atmospheric related ion mobility peaks, a daily maximum values of each peak and the time of occurrence were searched from the data. In Fig. 8a–i these daily maxima have been divided in four hours time slots and plotted separately for different measurement periods. The results show that some

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of the peaks followed certain daily pattern while some of them showed maxima values independent from the time of the day.

The clearest daily pattern was achieved for positive peaks P2 and P3 which both show more maxima values during evenings, nights and early mornings while midday and afternoon seems to be less active hours. This might indicate toward monoterpenes and monoterpene oxidation products which have been reported to have the highest concentrations during night time (Sellegrì et al., 2005; Rinne et al., 2005). For the positive peak P1 the trend was not as clear as they were for P2 and P3, but the peak P1 still showed an increasing trend towards the evening hours. According to studies of Rinne et al. (2005) trace gases such as methanol, acetone and butanol have the highest concentrations on late afternoons and lowest during the night. Sellegrì et al. (2005) reported acetone to have maxima between 10:00 and 12:00 and also around 21:00. These support the hypothesis that the peak P1 could be formed by acetone. For peak P4, a daily pattern was not observed but the days of occurrence is quite small for any conclusions. The peak A+NH<sub>3</sub> showed relatively stable daily patterns with slight increase in occurrence during night. In the case of A+NH<sub>3</sub> this might be due to the sticky nature of ammonia and amine compounds.

For negative peaks, the temporal behaviour of the peak PN1 shows how the occurrence of the maxima values dropped after early morning hours staying low until the evening when they started to rise again. The temporal behaviour of the peak PN2 was not that consistent between different measurement periods, but increasing trend towards evening and night hours with minimum in early mornings can be seen especially from the measurement period 2009. The peak PN0 was observed only during 0–12 but the total number of occurrence days was relatively low. For formic acid a daily pattern with low concentration at night time, increasing strongly in the morning and having a maximum in the afternoon, has been reported (Hofmann et al., 1997).

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### 3.4 Case-studies

Four different cases from the measurement period of 2009 were chosen for more detailed analysis. Each of these cases present a continuous measurement period of approximately three days and the cases were chosen so that each of them presents different atmospheric conditions in the gas and particle phase.

Case 1 (9–12 March 2009, Fig. 9a) shows a period of low particle concentration when particle formation does not occur (Fig. 9a upper panel). The corresponding ion mobility distribution was relatively simple with only reaction ions and couple of other weak peaks present (Fig. 9a lower panels). The slight downshift of the ion mobility peaks is caused by the sudden drop of app. 3 °C of the temperature in the drift chamber. The atmospheric temperature variation was minor varying between –2.5 °C and –5 °C. The IMS distribution was clean showing only a small amount of peaks other than the reaction ions simultaneously with the low measured particle concentrations. Thus during the measurement period of the Case 1, the air was relatively clean considering both the gas and particle phase.

Case 2 (27–30 March 2009, Fig. 9b) presents a polluted measurement period. The particle concentration was clearly higher than in Case 1 (Fig. 9b upper panel) as well as most of the trace gas concentrations. The wind was coming from more polluted areas (51–328 °) than in Case 1. The temperature varied between –9.9 and 0.9 °C but the effect of varying relative humidity and temperature was not, at least directly, seen in IMS distribution. The polluted air can be seen in higher particle concentrations as well as in rather rich and intense ion mobility peak distributions (Fig. 9b lower panels).

Case 3 (15–18 May 2009, Fig. 9c) presents a measurement period where new particle formation takes place every day. During this period the wind direction was mainly from North and North-East (340–156 °). Temperature was warming up compared to Cases 1 and 2 being now 2–16 °C. Most of the trace gases had lower concentrations than during other Cases. One noticeable fact from this measurement period is that the A+NH<sub>3</sub>-peak was detectable throughout the period. Also the peak P2 was detectable

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throughout the period showing bursts of stronger intensity directly after the particle formation. The first steps of particle formation process was seen as clean periods in the IMS distribution. When the nucleated particles grow the IMS distribution showed stronger peak intensities. One may speculate whether those peaks “have been there” but vanish from the distribution during the nucleation process because the new particle formation process consumes the trace gases in question, or they appear only later to support the growth of the particles.

Case 4 (27–30 April 2009, Fig. 9d) illustrates the difference between polluted and clean atmospheric conditions in connection with assumed changing of the air masses. Approximately the first half of the measurement period was the polluted part: particle concentration was relatively high as well as the trace gas concentrations (Fig. 9d upper panel). The temperature was varying between 0 and 20 °C without clear influence on ion mobility distribution. Quite suddenly the air mass changed and the particle concentration decreased dramatically. Same phenomenon can be seen at the same time in the ion mobility distribution both on positive and negative polarity (Fig. 9d lower panels). The ion mobility distributions changed so that there were not as many different ion mobility peaks present as there were during the polluted period and the intensities of the rest of the peaks decreased. Only the  $A+NH_3$  -peak was showing slightly stronger intensity during the clean period than during the polluted one. Case 4 showed most clearly how the IMS is capable of recognizing the overall cleanness of the prevailing atmospheric conditions and changes in situ.

## 4 Conclusion

The ion mobility spectrometer was implemented for direct, continuous atmospheric measurements without any pre-separation, purification, drying or heating of the sample air. The study showed that with this technique several different atmospheric related ion mobility peaks formed by different trace gas compounds can be distinguished from the measured ion mobility distribution. In this study, no clear correlation between

atmosphere related ion mobility peaks and common trace gases, meteorological parameters or radiation was achieved. This does not mean that there could not be a correlation between proper subsets of the data. More specific study of the possible correlations is left for future studies.

5 With the measurement concept used in this study, the IMS can be considered to be suitable for fast, on-line detection of overall cleanness of the prevailing air mass on site. It is possible to detect in situ the changes in air masses and trace gas compositions. The IMS showed a potential for detecting and measuring certain trace gas compounds, such as ammonia and amines. For this, the measurement concept should be tuned to  
10 detect only the compound under interest. Also the concentration calibration is required. The main challenge in concentration calibration is the characteristic feature of the IMS that the amount of the charge available is constant. This means that the intensity of an individual peak is always influenced by the concentrations of the other compounds present. Thus absolute concentration is rather challenging to be achieved with the  
15 measurement concept used here. For long term IMS-measurements directly from atmospheric air, the issue of drift gas conditioning and the changing humidity conditions should be recognized as well.

*Acknowledgements.* A.-K. V. acknowledges the Ministry of Education and the Academy of Finland (project No. 118780) and the Finnish Concordia fund for funding. The financial support by  
20 the Academy of Finland Centre of Excellence program (project no. 1118615) and EU-project EUCAARI (European Integrated project on Aerosol Cloud Climate and Air Quality interactions, project no. 036833-2) is gratefully acknowledged. M. K. acknowledges support from the European Research Council Advanced Grant (no. 227463).

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**Table 1.** Atmosphere related ion mobility peaks traced in this study, their computational properties and hypothetical origin with different literature values.

Positive peaks	Measured peak	Computational values		Hypothetic origin with literature values		
	Reduced mobility value [ $\text{cm}^2(\text{Vs})^{-1}$ ]	Mean peak value [ $\text{cm}^2(\text{Vs})^{-1}$ ]	Mass app. [amu]	Reduced mobility value [ $\text{cm}^2(\text{Vs})^{-1}$ ]	Mass [amu] <sup>†</sup>	PA [ $\text{kJ}(\text{mol})^{-1}$ ] <sup>‡</sup>
Ammonia + amine (A+NH <sub>3</sub> )	2.28–2.45	2.36	39 ± 8	2.33 (NH <sub>3</sub> ) <sup>1</sup> 2.46 (DMA) <sup>2</sup> 2.02 (DMA) <sup>3</sup> 2.25 (TMA) <sup>1</sup> 2.36 (TMA) <sup>2</sup>	17 (NH <sub>3</sub> ) 45 (DMA) 59 (TMA)	854 (NH <sub>3</sub> ) 930 (DMA) 949 (TMA)
Reaction ion peak (RIP)	2.03–2.19	2.11	57 ± 12	2.20 <sup>1</sup>	18 (H <sub>2</sub> O) 71 O <sup>+</sup> (H <sub>2</sub> O) <sub>3</sub>	691 (H <sub>2</sub> O)
Peak 1 (P1)	1.82–1.66	1.74	101 ± 21	1.88 (C <sub>3</sub> H <sub>6</sub> O) <sup>3</sup> 1.78 (C <sub>3</sub> H <sub>6</sub> O) <sup>6</sup>	58 (C <sub>3</sub> H <sub>6</sub> O)	812 (C <sub>3</sub> H <sub>6</sub> O)
Peak 2 (P2)	1.68–1.47	1.57	132 ± 27	1.59 ( $\alpha$ -pinene oxidation product) <sup>5</sup>	–	–
Peak 3 (P3)	1.48–1.32	1.40	179 ± 36	–	–	–
Peak 4 (P4)	1.31–1.12	1.21	254 ± 51	–	–	–
Negative peaks	Reduced mobility value [ $\text{cm}^2(\text{Vs})^{-1}$ ]	Mean peak value [ $\text{cm}^2(\text{Vs})^{-1}$ ]	Mass app. [amu]	Reduced mobility value [ $\text{cm}^2(\text{Vs})^{-1}$ ]	Mass [amu] <sup>†</sup>	PA [ $\text{kJ}(\text{mol})^{-1}$ ] <sup>‡</sup>
Peak 00 (PN00)	– (2.84–2.66)	–2.75	23 ± 5	–	–	–
Peak 0 (PN0)	– (2.54–2.51)	–2.52	31 ± 7	–	–	–
Reaction ion peak (RIN)	– (2.51–2.26)	–2.39	38 ± 8	– (1.99–2.09) <sup>7</sup>	32 (O <sub>2</sub> ) 49 (O <sub>2</sub> <sup>-</sup> (H <sub>2</sub> O))	421 (O <sub>2</sub> )
Peak 1 (PN1)	– (2.26–2.16)	–2.21	49 ± 10	– (Formic acid) – (Acetic acid) – (NO <sub>3</sub> <sup>-</sup> )	46 60 62	742 784 591
Peak 2 (PN2)	– (2.09–1.92)	–2.01	67 ± 14	– (Propionic acid)	74	797

<sup>1</sup> Mäkinen et al. (2011),  $T \sim 70^\circ\text{C}$ , in air. <sup>2</sup> Karpas (1989),  $T \sim 200^\circ$ , in air. <sup>3</sup> Eiceman and Karpas (2005),  $T \sim 50^\circ\text{C}$ , in N<sub>2</sub>. <sup>4</sup> Haynes (2011). <sup>5</sup> Viitanen et al. (2010),  $T = 30^\circ\text{C}$ , in air. <sup>6</sup> Rudnicka et al. (2010),  $T = 23^\circ\text{C}$ , in N<sub>2</sub>. <sup>7</sup> Bocos-Bintintan et al. (2001),  $T = 20^\circ\text{C}$ , in air.

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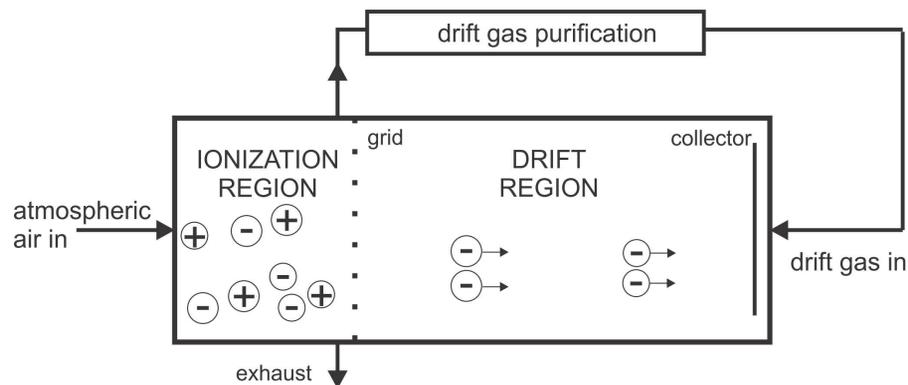


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**Fig. 1.** Operation principle of the IMS based on time-of-flight method with internal drift gas purification.

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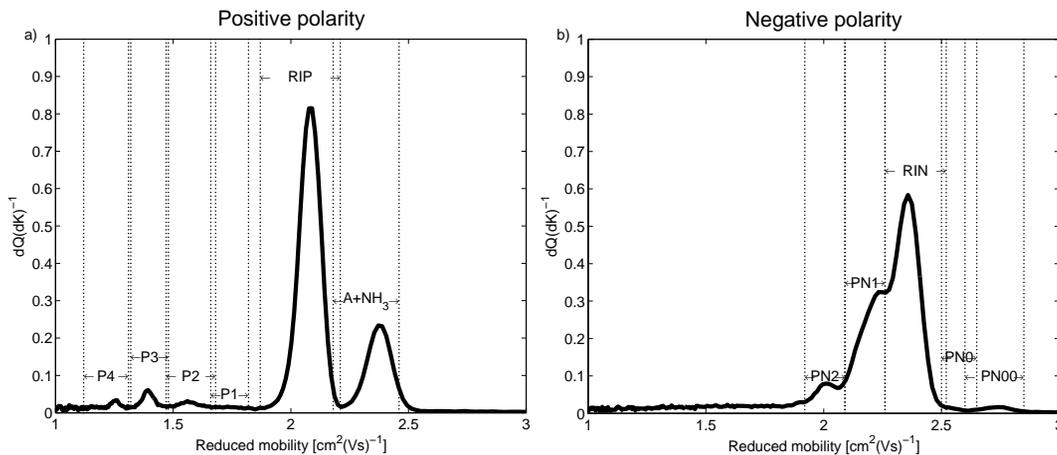
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**Fig. 2.** Typical positive (a) and negative (b) ion mobility spectrum. The reduced mobility limits that were used for tracing the ion mobility peaks have been indicated in the spectra.

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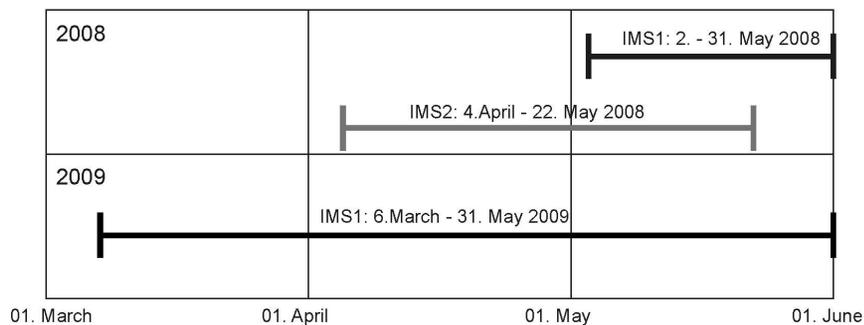
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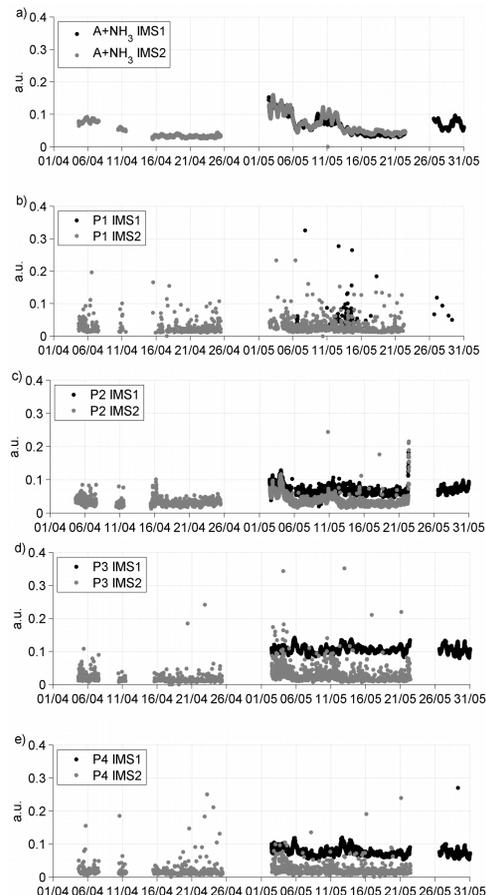
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**Fig. 3.** Studied measurement periods for two different ion mobility spectrometers.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Fig. 4.** The normalized peak intensities of positive ion mobility peaks measured with IMS1 (black dots) and IMS2 (grey dots) during 2–31 May 2008 in Hyytiälä. If the signal is not shown either the concentration of the trace gas is below detection limit or a measurement break has occurred.

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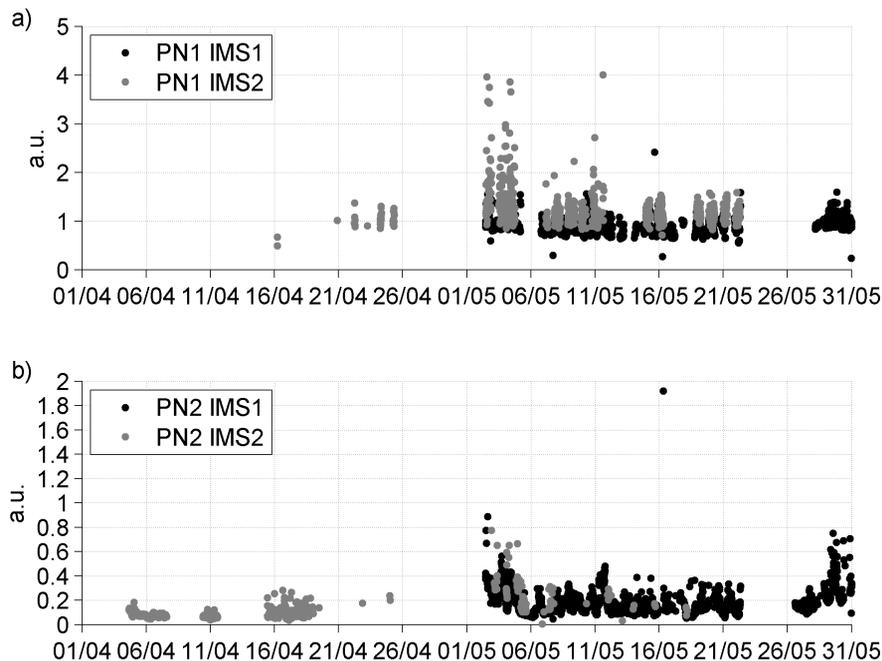
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**Fig. 5.** The normalized peak intensities of negative ion mobility peaks measured with IMS1 (black dots) and IMS2 (grey dots) during 2–31 May 2008 in Hyytiälä. If the signal is not shown either the concentration of the trace gas is below detection limit or a measurement break has occurred.

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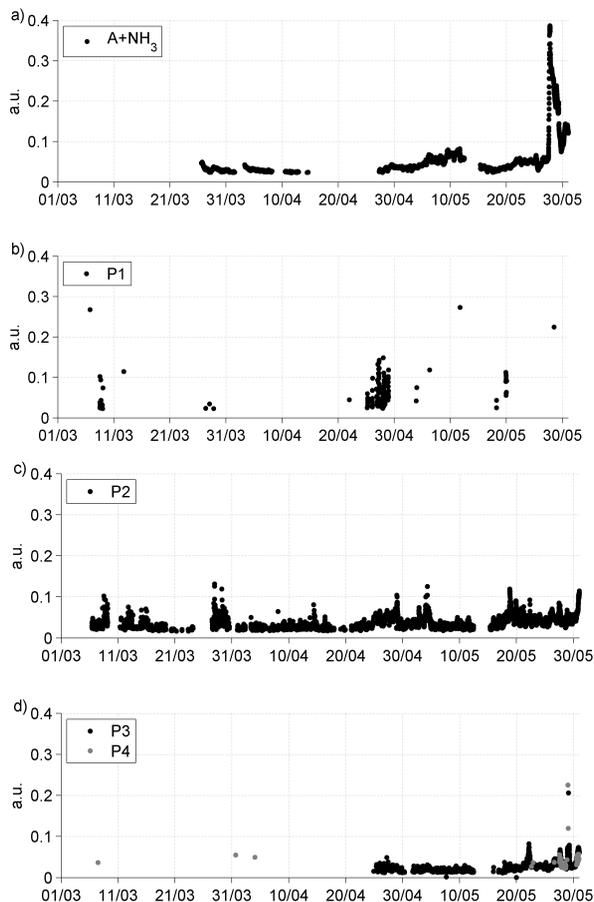
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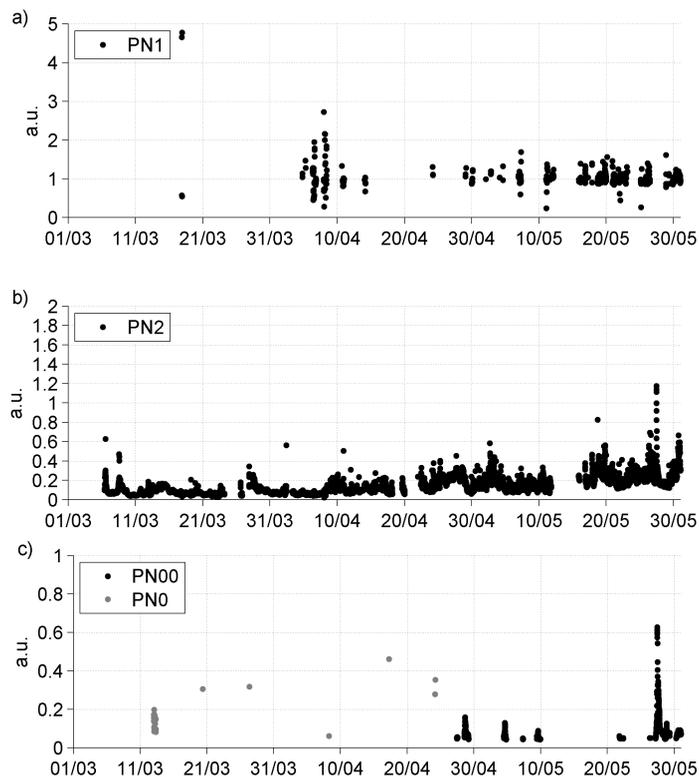
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**Fig. 6.** The normalized peak intensities of positive ion mobility peaks measured with IMS1 during 1 March–31 May 2009 in Hyytiälä. If the signal is not shown either the concentration of the trace gas is below detection limit or a measurement break has occurred.

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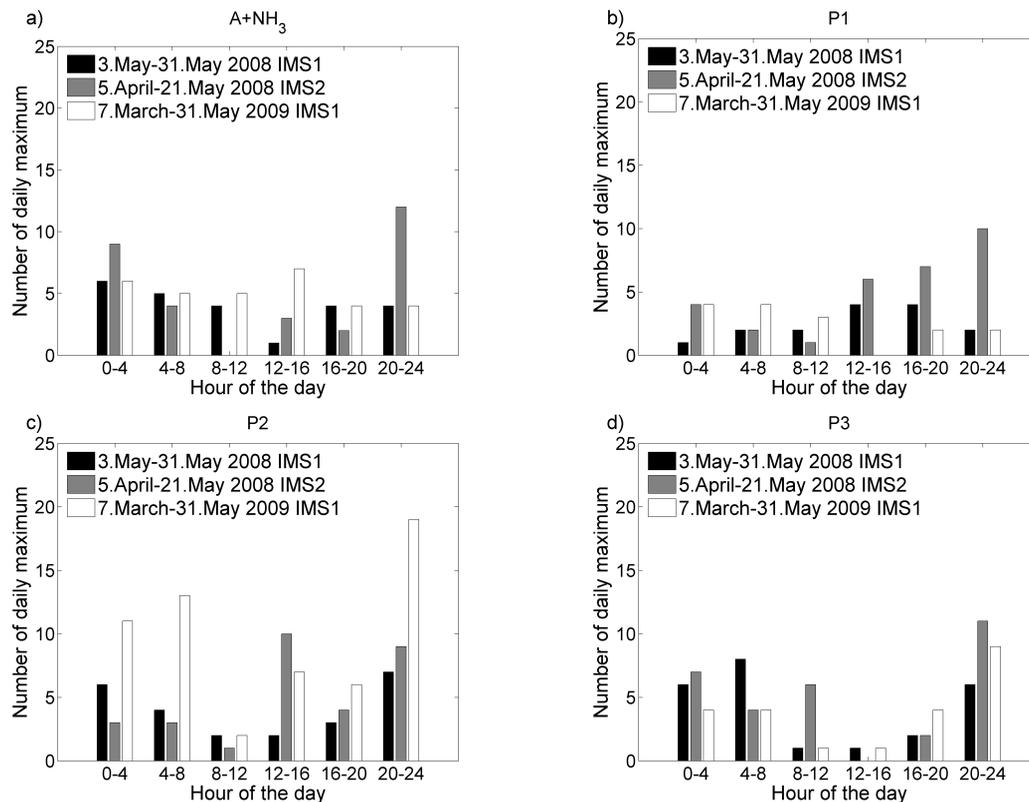
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**Fig. 7.** The normalized peak intensities of negative ion mobility peaks measured with IMS1 during 1 March–31 May 2009 in Hyytiälä. If the signal is not shown either the concentration of the trace gas is below detection limit or a measurement break has occurred.

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**Fig. 8.** Temporal behaviour of the measured ion mobility peaks.

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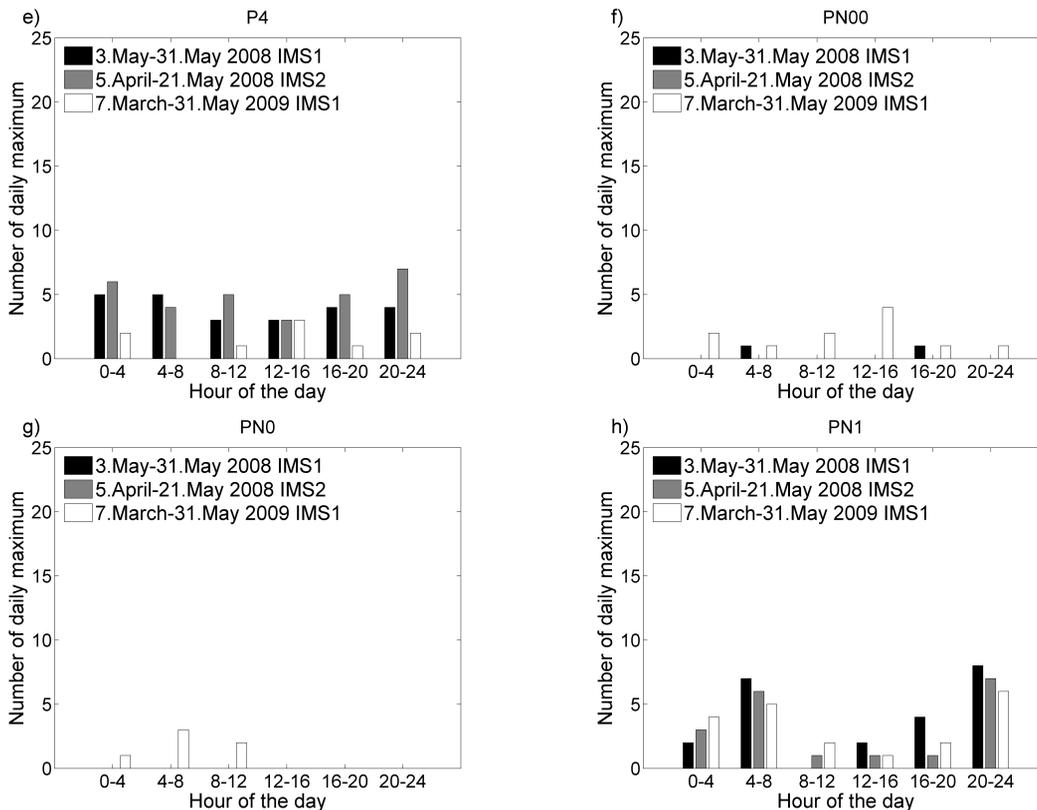


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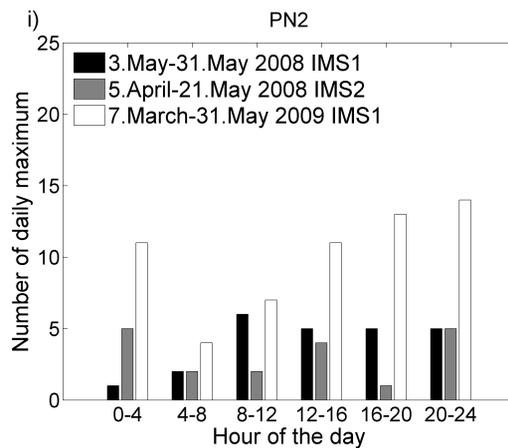
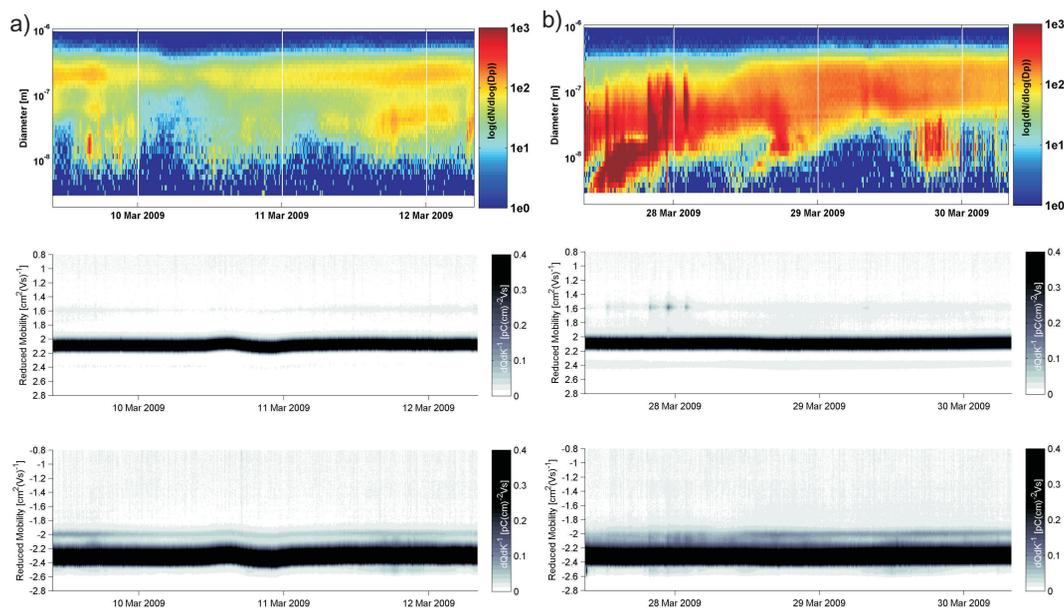


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**Fig. 9.** Case 1: 9–12 March 2009 (a), case 2: 27–30 March 2009 (b), case 3: 15–18 May 2009 (c) and case 4: 27–30 April 2009 (d). The uppermost panels in a–d present the particle distributions, the middle mosts the positive ion mobility distributions and the under mosts negative ion mobility distributions from the same three day time period.

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## Atmospheric trace gas measurements using IMS

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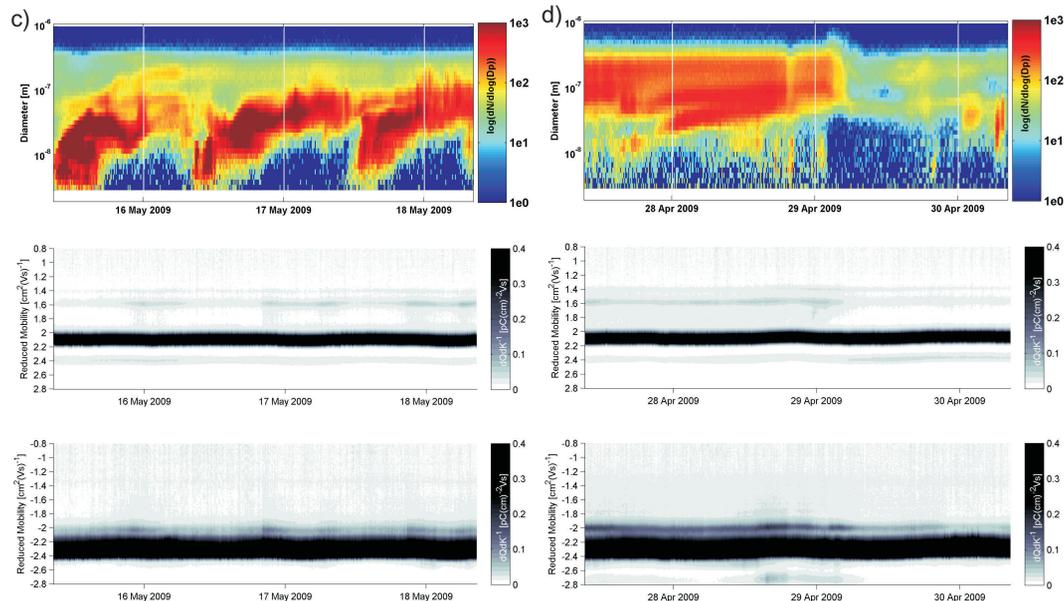


Fig. 9. Continued.

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