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Variability of air ion concentrations in urban Paris

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Abstract

Air ion concentrations influence new particle formation and consequently the global aerosol an cloud condensation nuclei loads. We aimed to evaluate air ion concentrations and characteristics of new particle formation events (NPF) in the megacity Paris, France (Megapoli project). We measured air ion number size distributions (0.8–42 nm) and fine particle number concentrations (> 6 nm) in an urban site of Paris between 26 June 2009 and 4 October 2010. Air ions were size classified as small (0.8–2 nm), intermediate (2–7 nm) and large (7–20 nm). The media concentrations of small and large ions were 670 and 680 cm^{-3} respectively (sum of positive an negative polarities) whereas the median concentration of intermediate ions was only 20 cm^{-3}, as these ions were mostly present during new particle formation bursts, i.e. when gas-to-particle conversion produced fresh aerosol particles from gas phase precursors. During peaks in traffic-related particle number, the concentrations of small and intermediate ions decreased whereas the concentrations of large ions increased. Seasonal variations affected the ion population differently, with respect to their size and polarity. NPF was observed in 13 the days, being most frequent in spring and late summer (April, May, July and August). The results also suggest that NPF was favoured on the weekends in comparison to workdays, likely due to the lower levels of condensation sinks in the mornings of weekends (CS weekdays 09:00: $18 \times 10^{-3}\,s^{-1}$; CS weekend 09:00: $8 \times 10^{-3}\,s^{-1}$). The median growth rates (GR) of ions during the NPF events varied between 3–7 $nm\,h^{-1}$, increasing with the ion size and being higher on workdays than on weekends for intermediate and large ions. The median GR of small ions on the other hand were rather similar on workdays and weekends. In general, NPF bursts changed the diurnal cycle of particle number, intermediate and large ions by causing an extra peak between 09:00 and 14:00. On average, during the NPF bursts the concentrations of intermediate ions were 8.5–10 times higher than on NPF non-event days, depending on the polarity, and the concentrations of large ions and particles were 1.5–1.8 and 1.2 times higher, respectively. Because the median concentrations of intermediate ions

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were considerably higher on NPF event days in comparison to NPF non-event days, the results indicate that intermediate ion concentrations could be used as an indication for NPF in Paris. The results suggest that NPF was a source of ions and aerosol particles in Paris and therefore contributed to both air quality degradation and climatic effects, especially in the spring and summer.

1 Introduction

In the last decade, with the threat of climate change, a growing number of researchers have focused on understanding the association between aerosol particles and the climate. Aerosol particles are either directly emitted into the atmosphere (primary particles) or formed in the atmosphere (secondary particles). Freshly formed secondary aerosol particles can grow within a day or two to cloud condensation nuclei (CCN) sizes and affect the radiation budget of the Earth (Makkonen et al., 2012; Kerminen et al., 2012; Wiedensohler et al., 2009). Merikanto et al. (2009) estimated that 45 % of the global tropospheric CCN at 0.2 % super saturation are originated from secondary particle formation. In addition to the climatic effects, the formation and growth of secondary aerosol particles contributes to the deterioration of the air quality as aerosol particles are associated to adverse health effects (Oberdörster et al., 2005). Despite its importance the mechanisms underlying secondary new particle formation are not yet fully understood (see Kulmala et al., 2014). In the atmosphere, new particle formation occurs in different steps including formation of low volatile vapours, clustering of vapour molecules and subsequent growth (see Kulmala et al., 2014). The presence of air ions facilitates the formation and growth of new particles by aiding the stabilization of the molecular clusters during the initial stages of nucleation (ion-induced nucleation) (e.g. Yu and Turco, 2000). The magnitude of the contribution of ions to new particle formation (NPF) however is still under investigation. On one hand, several studies reported a rather low contribution of ion-induced nucleation to the total NPF events, 10–30 % (Hirsikko et al., 2011, and references therein), with even lower values observed in ur-

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ban areas, 0.2–1.3 % (Gagné et al., 2012; Iida et al., 2006; Herrmann et al., 2014). On the other hand, some models and chamber studies suggest that ion-mediated nucleation (which considers ion-ion recombination) may be a significant path for NPF (Yu and Turco, 2011; Yu, 2010; Svensmark et al., 2007; Nagato and Nakauchi, 2014; Kirkby et al., 2011; Riccobono et al., 2014).

Ions are always present in the air and are responsible for the atmospheric electrical conductivity. They are mainly formed from ionizing radiation of decaying radon, gamma radiation and galactic cosmic radiation (e.g. Hirsikko et al., 2011). Thunderstorms and water splashing also contribute to the formation of air ions in the atmosphere (Hirsikko et al., 2011; Tammet et al., 2009). The most important sinks for ions are ion-ion recombination to form neutral particles, and attachment to pre-existing aerosol particles (Kamsali et al., 2011; Hirsikko et al., 2011).

Urban areas are important sources for global aerosol and CCN load because they emit both primary particles and precursors for secondary particle formation. Nevertheless, the number of studies focusing on the behaviour of air ions and particularly its association to NPF in urban areas around the world is still somewhat limited (e.g. Tiitta et al., 2007; Hirsikko et al., 2007b; Retalis et al., 2009; Tammet et al., 2014; Gagné et al., 2012; Herrmann et al., 2014; Backman et al., 2012; Crilley et al., 2014; Jayaratne et al., 2010, 2014; Ling et al., 2013, 2010; Siingh et al., 2013; Lee et al., 2012; Iida et al., 2006, 2008; Pikridas et al., 2015), and actually only some of them measured ion size distributions. The main aim of this study was to determine the frequency and seasonal variations of NPF events in a megacity based on AIS measurements. Our research was developed within the framework of the project: megacities: emissions, urban, regional and Global Atmospheric Pollution and climate effects, and Integrated tools for assessment and mitigation (MEGAPOLI), which aimed to improve the understanding of the impacts of megacities on the climate. In this context, Paris, one of the largest cities in Europe, was chosen as case study. Although some publications on aerosol particles in Paris already exist (e.g. Crippa et al., 2013; Freutel et al., 2013; Freney et al., 2013; Sciare et al., 2010; Pikridas et al., 2015), only Pikridas et al. (2015) considered air ion

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number size distributions (> 0.8 nm), which allows the evaluation of ion number concentrations in early stages of NPF. Pikridas et al. (2015) provided valuable information on the spatial variation of NPF events and particle number concentrations as well as on factors affecting NPF in Paris and surrounding areas, however, the study was based on rather short campaigns (about two months of data) and air ion number size distributions were used only for NPF event classification, duration and frequency purposes. Our study complements Pikridas et al. (2015) by providing detailed information on the behaviour of air ion concentrations of both polarities in three different size ranges, and particle number concentrations in Paris for over one year.

2 Materials and methods

We measured air ion size distributions (0.8–42 nm) and aerosol particle number (6–740 nm) at an urban background site in Paris from 26 June 2009 to 4 October 2010, using an Air Ion Spectrometer (AIS), and a combination of a Twin Differential Mobility Particle Sizer (TDMPS) and condensation particle counter (CPC). In addition to seasonal variations and frequency of NPF events, we also analysed seasonal variations and diurnal cycles of air ions and aerosol particles on workdays and weekends, and on NPF event and NPF non-event days. Furthermore, we estimated the average condensation sinks, and the growth rates of ions on workdays and weekends, and provided a statistical summary of air ions and aerosol particle number concentrations in Paris.

2.1 Description of the site

Paris is a megacity with 12.2 million inhabitants in its urban area (2.2 million in the centre alone) (INSEE, 2010a, b). Our measurements of air ion size distributions and particle total number concentrations were located at the Laboratoire d' Hygiène de la Ville de Paris building (LHVP) on 13 Arrondissement (latitude 48.83°; longitude 2.36°) in Paris (Fig. 1), from July 2009 to October 2010. Particle number size distributions were

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measured from a container on the ground of the LHVP building whereas air ion size distributions were measured on top of the building (about 15 m high). LHVP is located about 400 m away from busy intersections and is considered an urban background site (Sciare et al., 2010; Favez et al., 2007). The site was surrounded by a small street, a park and restaurants (Freutel et al., 2013). According to Crippa et al. (2013), important anthropogenic sources of particles in the site are traffic, cooking (from restaurants around noon and evenings), and biomass burning in general, whereas an important natural source is secondary particle formation.

2.2 Description of the instruments

2.2.1 Air ion number size distributions

We used an Air Ion Spectrometer (AIS, Airel Ltd.) (Mirme et al., 2007) to measure the size distributions of naturally charged particles and ions of both polarities simultaneously during 26 June 2009–4 October 2010 in Paris, France. The AIS comprises of two identical Differential Mobility Analysers (DMA), one for each polarity. The inner cylinder of the DMA is divided into four sections to which high voltages of varying intensities are applied. The outer cylinder of the DMA contains 21 electrically isolated electrodes, each connected to an individual electrometer collection ring. If a positive or negative voltage is applied to the inner cylinder, charged particles of the same polarity are repelled towards the electrometer rings of the outer cylinder, and the electrical currents generated are recorded. Thus, particle size is estimated based on the electrical mobility of the particle in the electric field, whereas particle number concentration is calculated based on the intensity of the currents measured by the electrometer. The AIS measures electrical mobilities varying from 3.2 to 0.0013 $cm^2 V^{-1} s^{-1}$, which is equivalent to mobility diameters of 0.8–42 nm (Asmi et al., 2009).

The main sampling line of the AIS was 0.6 m long (inner diameter: 35 mm) with a total inlet flow rate of 60 $L min^{-1}$ which was equally divided between both DMAs. A metallic grid was used in front of the inlet to prevent for instance large dust particles to enter

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the system. The sheath air flow of the DMAs was cleaned using corona chargers and electrical filters, and reused in a closed loop at 60 $\mathrm{L\,min^{-1}}$ (Gagné et al., 2011). Before each particle number size distribution was measured, the system was verified for natural background currents (due to instrumental noise) and these currents were subtracted from every measurement (Mirme et al., 2007). The instrumental setup and calibration are described in more details by Mirme et al. (2007) and Asmi et al. (2009), respectively. The accuracy of the particle number concentration of the AIS was estimated to be 10 %, which was mainly due to flow rate uncertainties (Mirme et al., 2007). During the campaign the accumulating air pollution inside the instrument causes decreasing flow rates between the maintenance periods. This may further increase the uncertainty of measured particle size and number especially at the larger end of the measured spectra.

2.2.2 Number size distributions and total concentrations of fine aerosol particles

We used a Twin Differential Mobility Particle Sizer (TDMPS) to measure the particle number size distribution (diameter 3–740 nm) during July 2009. The instrument comprised of a neutralizer, two Hauke DMAs (lengths: 110 and 280 mm; both with inner and outer diameters of 50 and 67 mm, respectively) and two condensation particle counters (CPC), models TSI 3025A (d_{50} : 3 nm, accuracy ± 10 % at $10^5\ \mathrm{cm^{-3}}$) and TSI 3010 (d_{50} : 10 nm, accuracy ±10 % at $10^4\ \mathrm{cm^{-3}}$). In the TDMPS, the aerosol particles were charged by the neutralizer, size-classified by the DMA, and optically counted by the CPC. The first DMA classified particles from 3–72 nm, while the second DMA classified particles from 25–740 nm. The sampling and sheath flow rates were 2 and 20 $\mathrm{L\,min^{-1}}$ respectively for the first DMA, and 0.5 and 5 $\mathrm{L\,min^{-1}}$ for the second DMA. The calibration of the TDMPS was done using polystyrene latex spheres (PSL) of diameters varying from 200 to 500 nm. The sampled air was dried using an automated diffusion dryer (Tuch et al., 2009). According to Wiedensohler et al. (2012) the drier is estimated

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to cause about 28 and 8 % of losses for particles of 3 and 10 nm, respectively, for the given flow rate through the drier. The TDMPS data was averaged per hour.

We also measured the total number concentration of fine aerosol particles by using a condensation particle counter (CPC, TSI 3772, dp_{50} : 6 nm, accuracy ±10 % at 10^4 cm^{-3} and ±20 % at 5× 10^4 cm^{-3}) during 11 August 2009–4 October 2010. In order to reduce the cut-off diameter from typical 10 to 6 nm, the condenser of the CPC was operated at 10 °C instead of the common operational temperature of 22 °C. The sampled air was dried using a Nafion dryer.

2.3 Data treatment and definitions

Air ion data containing negative concentrations (positive ions: 0.64 %; negative ions: 1.18 %), concentrations measured during unstable flow rates (optimum range: 1000 $cm^3 s^{-1}$ ± 8 %) and very noisy data were considered invalid. A three-point median filter was applied to the ion concentrations to reduce noise as suggested by Kulmala et al. (2012). The air ions were mobility-classified as small or cluster ions (1.3–0.5 $cm^2 V^{-1} s^{-1}$), intermediate (0.5–0.034 $cm^2 V^{-1} s^{-1}$) and large ions (0.034–0.0042 $cm^2 V^{-1} s^{-1}$), which correspond to mobility diameters of 0.8–2, 2–7 and 7–20 nm, respectively (Mäkelä et al., 1996).

The particle total number concentrations for the entire campaign were obtained by combining the total concentrations measured by the TDMPS (calculated from 6 to 740 nm, 1 h means, period: 1–31 July 2009) with the concentrations measured by the CPC (> 6 nm, 1 h means, period: 11 August 2009–4 October 2010). Total concentrations below 100 cm^{-3} were considered invalid as these values are unrealistic for urban areas.

To analyse the behaviour of the ion population during NPF we plotted air ion size distributions as a function of time, from 27 June 2009 to 3 October 2010. Based on the plots we classified the days into NPF events, NPF non-events or undefined days according to the procedure described by Hirsikko et al. (2007a). NPF event days referred to days where new particle formation and growth was clearly observed for several

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hours; NPF non-event days comprised days of no particle formation, and undefined days referred to days in which the occurrence of NPF was unclear.

The growth rates of ions were calculated based on the maximum-concentration method described in Kulmala et al. (2012): (1) we manually selected the time of peak concentrations during NPF for each particle size range, (2) applied a Gaussian fit to the manually selected peak to determine the time of maximum concentration of that particle size range, and (3) calculated the GR by linear regression (least-square fit) to the particle size vs. maximum concentration time data points.

Condensation sink (CS) was calculated based on the equations described by Dal Maso et al. (2005) using dry particle number size distributions. The approach estimates the loss rate of the condensable vapours during the change from the gas-to-particle phase (Kulmala et al., 2001). A high CS indicates the presence of large number of aerosol particles acting as both condensing nucleus for vapours and coagulation surfaces.

Months were classified into seasons as follows: winter: December, January and February; spring: March, April and May; summer: June, July and August; autumn: September, October and November. The air ion data was originally averaged every 3 min, however, as the particle number data from the TDMPS was provided as hourly means, to facilitate comparison the air ion data and the particle number concentration data from the CPC were also presented as hourly means. The only exceptions were Fig. 6a–d and Fig. A2, where the air ion data was shown in the original format (3 min means). Moreover, all the data in this study was presented as UTC (Paris local time: UTC + 1 h in the winter, and UTC + 2 h in the summer), and when calculating concentrations on workdays and weekends, national holidays were classified as weekends.

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3 Results and discussion

3.1 Concentrations of ions and particles at the LHVP site

The median of the daily means, and the median of the hourly means of particle number concentration in the LHVP were 12 900 cm^{-3} (data not shown) and 12 500 cm^{-3} (Table 1), respectively. Aalto et al. (2005) and Puustinen et al. (2007) observed daily medians of particle number concentrations ranging from 9000–38 500 cm^{-3} (both studies combined) in urban background sites of European cities, including Augsburg, Stockholm, Helsinki, Amsterdam, Birmingham, Athens, Barcelona and Rome. The mean particle number concentrations in urban and suburban areas of São Paulo, Nanjing and Beijing were 23 500, 23 000 and 23 900–32 800 cm^{-3} (combined studies), respectively (Backman et al., 2012; Herrmann et al., 2014; Wu et al., 2008; Wang et al., 2013). Thus, particle number concentrations in Paris (LHVP) were in range with the daily medians of other European cities and were lower roughly by a factor of two (mean: 13 700 cm^{-3}) compared to busy cities of other continents. Pikridas et al. (2015) evaluated mean particle number concentrations during the summer and winter in the LHVP site and reported similar concentration for particles of 10–500 nm (mean of both seasons: 13 500 cm^{-3}). In general, particle number concentrations tend to vary considerably among cities due to differences in meteorology, spatial and temporal distribution of local sources, emission-cleaning technologies and air quality regulations.

The mean number concentrations of small ions at the LHVP site were 330 and 390 cm^{-3} for positive and negative polarities, and are close to the lower range reported in the review by Hirsikko et al. (2011) for sites around the world, 200–2500 cm^{-3}. Shortly after formation the small ions are removed from the air by ion-recombination and by coagulation with larger particles, thus in polluted environments, where the load of aerosol particles is high (leading to condensation sink), the concentrations of small ions are often lower than in cleaner environments (Hirsikko et al., 2011, and references therein, 2007b; Tiitta et al., 2007).

In Nanjing, China, the total concentration of small ions, aerosol particles and CS were 840 cm^{-3} (sum of polarities), 23 000 cm^{-3} and 5.4×10^{-2} s^{-1}, respectively (Herrmann et al., 2014). Considering only the period of July 2009 and 15 January/15 February 2010, when CS calculations were possible, the mean small ion concentrations, particle number and CS in LHVP were 800, 14 460 cm^{-3} and 1.43×10^{-2} s^{-1}, respectively. The small ion concentrations in Nanjing were similar to that of the LHVP despite the considerably higher particle total number and CS in Nanjing. The large particle surface area acting as coagulation and condensation sinks in Nanjing should result in lower concentrations of small ions in comparison to LHVP. Since this was not observed, the results suggest that Nanjing may have a higher production rate of small ions than Paris. Other studies around the world reported mean and median concentrations of small ions to be in range with the observed in LHVP, varying from 183–860 cm^{-3} for positive and 151–720 cm^{-3} for negative ions near traffic and in urban background sites of cities such as Athens (Greece), Kuopio (Finland), Helsinki (Finland) and Brisbane (Australia) (Retalis et al., 2009; Tiitta et al., 2007; Hirsikko et al., 2007b; Ling et al., 2013).

The concentrations of intermediate ions were in general very low and were mostly present on NPF event days in comparison to NPF non-event days (Sect. 3.5). The mean concentrations of intermediate ions during the whole campaign were 20–30 cm^{-3} per polarity, and were similar to the annual mean observed by Tammet et al. (2014) in the city of Tartu, Estonia, 35–40 cm^{-3} (per polarity), but roughly half of the observed by Tiitta et al. (2007) (40–70 cm^{-3} per polarity) near a road in Kuopio, Finland. One explanation for the higher concentrations in Kuopio could be the proximity of the road, as some studies (Jayaratne et al., 2010; Ling et al., 2013, 2010; Lee et al., 2012) reported ion concentrations near traffic to be higher than in sites away from traffic.

The median concentrations of positive and negative large ions were 410 and 270 cm^{3}, respectively. In Helsinki, Hirsikko et al. (2007b) reported weekday median concentrations of large ions (10–40 nm) of 510 and 540 cm^{-3} for positive and negative polarities, respectively. When the hourly data was segregated into workdays and weekends the weekday concentrations of large ions (10–40 nm) were 1220 and 850 cm^{-3},

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for positive and negative polarity, thus considerably higher than the observations in Helsinki. As the concentrations of large ions are influenced by traffic related aerosols (Hirsikko et al., 2007b; Tiitta et al., 2007), the difference in large ion concentrations could be due to a larger number of sources of aerosol particles, i.e. vehicle emissions, in LHVP surroundings in comparison to Helsinki.

In July 2009, 41 % of the total particles in the size range of 3–23 nm comprised of naturally charged particles (sum of positive and negative polarities). The month-to-month median concentrations of ions from 0.8 to 42 nm varied between 1000–2000 cm^{-3} $polarity^{-1}$ (data not shown).

Figure A1 shows correlations between particle number and ions. Particle number correlated the highest with large ions of both polarities (r = 0.58–0.61, $p < 0.01$) as expected, since it is very likely that these aerosol particles were in charge balance most of the time (aerosol particles quickly attach to ions forming large ions). Weak or no correlation was found between particle number and small or intermediate ions ($r < |0.18|$, $p < 0.01$). Accumulation mode aerosol particles that have large surface area (thus creating high condensation sinks) and small ions are often negatively associated as the first act as sink for the latter. Aerosol particles in urban areas are mainly originated from human activities such as traffic, while small ions are originated from natural ionizing radiation, hence the weak correlation.

3.2 Diurnal cycles and number size distributions of ions

Figure 2 shows the diurnal variations of ions and particle number concentrations. On workdays, particle number concentrations peaked in the morning (07:00–08:00) and in the evening (19:00–20:00) (Fig. 2g) reflecting traffic rush hours. This pattern was consistent with the findings of Pikridas et al. (2015) in Paris during summer and winter. The evening peak was fairly constant regardless of the day, whereas the morning peak on workdays was about 50–60 % higher than on the weekends, when traffic intensity is generally lower. The constant presence of an evening peak suggests constant nocturnal activities in the area, e.g. traffic and/or cooking emissions from restaurants as

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suggested by Freutel et al. (2013). A decrease in boundary layer mixing height also plays a role in accumulating air pollutants in the evening due to poor dilution, as suggested by Pikridas et al. (2015). Cimini et al. (2013) shows that the mixing height of the boundary layer in 15 August 2011 in SIRTA, a site 20 km away from LHVP, increased at 08:00 and decreased at 18:00 (UTC), roughly the time when the evening peak begins.

Large ions had maximum median concentrations of 400–600 cm^{-3} per polarity and a diurnal cycle very similar to that of particle number (Fig. 2e–f), undergoing an abrupt increase from the night to the morning rush hours and from weekends to workdays. As traffic produces aerosol particles, the concentrations of large ions are likely resulting from the coagulation between neutral aerosol particles and small or intermediate ions. Because busy intersections were located about 400 m away, it is possible that particulate traffic emissions from the intersections enhanced concentrations of large ions in LHVP. Note that as the instruments measuring particle number and ions overlap from 6–20 nm, some of the intermediate and all of the large ions were also detected by the CPC. If we compare the diurnal cycle of particle number concentrations to that of large ions (sum of polarities), the latter comprised about 5.5 % of the total particle number concentrations in the morning of workdays.

Small ion number concentrations of both polarities peaked early in the morning (Fig. 2a and b) and decreased during the day in agreement with some studies reviewed by Hirsikko et al. (2011). The higher concentrations on early mornings may be attributed to both the accumulation of ionizing radiation from radon decay, as the boundary layer mixing height is usually lower before sunrise (Hirsikko et al., 2011), and the lower number of condensation sinks early in the mornings (Fig. A3), which decrease the removal rate of small ions.

On workdays, the peak median number concentrations of small ion were between 380–430 cm^{-3} per polarity. On weekends, the number concentrations of small ions were slightly higher (400–490 cm^{-3}) and the elevated concentrations of positive small ions lasted a few hours longer than on workdays, indicating that the production rate of small ions (i.e. from radon radiation) was similar throughout the week but the removal rates were lower on weekends (lower level of coagulation sink). The simultaneous decrease in small ion concentrations and increase in large ion concentrations and particle number (Fig. 2e–g) suggests that part of the small ion population was lost by attachment to aerosol particles as observed in previous studies (Hirsikko et al., 2007b; Jayaratne et al., 2014). The concentrations of positive small ions in the mornings of workdays (07:00) were about 26 % lower in comparison to the mornings of weekends (07:00) indicating that this fraction may have been lost by coagulation to pre-existing aerosol particles.

The median number concentrations of intermediate ions (Fig. 2c and d) were once again low and were considerably different from the mean indicating a large variability. On workdays, the median concentrations of positive intermediate ions showed two peaks (04:00–05:00 and 12:00–13:00), while in the weekends only one shallow peak was observed. The decrease in concentrations of intermediate ions in the mornings of workdays between 06:00 and 08:00 coincided with the peak in particle number and CS (Fig. 2 and A3), indicating that coagulation sinks from traffic emissions scavenged the intermediate ions. On weekends, with the decrease in the number of aerosol particles, the number concentrations of intermediate ions remained elevated for several hours. Thus, NPF along with the decrease of particle number concentrations (condensation sinks) in the afternoon enhanced concentrations of intermediate ions around 12:00–13:00. As intermediate ions are directly associated to NPF, the results indicate that NPF was more likely to occur on weekends than on workdays in LHVP. Negative intermediate ions showed a similar diurnal cycle as the positive intermediate ions, only with lower concentrations. Despite the effects of traffic on the ion number concentrations, traffic intensity did not seem to influence the median ion size distribution (Fig. A2) in agreement with Tiitta et al. (2007).

Studies near busy roads (10–100 m away) in Finland reported that traffic emissions caused a decrease in small ion concentrations and an increase in both intermediate and large ions (Hirsikko et al., 2007b; Tiitta et al., 2007) which agrees with our results for small and large ions but disagree for intermediate ions. In Helsinki, the weekday diurnal peak concentrations of small, intermediate and large ions were roughly 750–900 cm^{-3}, 80–90 cm^{-3} and 950–1000 cm^{-3}, respectively per polarity. The number concentrations were thus higher in Helsinki despite similar CS range between the sites (Helsinki: 1– 50× 10^{-3} s^{-1}, LHVP: 1.7–51× 10^{-3} s^{-1}). The discrepancy is likely caused by higher radon decay and gamma radiation emissions rates from soils in Helsinki. The World Health Organization estimates higher levels of indoor radon emissions in Finland (120 Bq m^{-3}) than in several other European countries, including France (89 Bq m^{-3}) (WHO, 2009). In addition to differences in radon emission rates, the size-classification of intermediate and large ions in Hirsikko et al. (2007b) (3–10 and 10–40 nm, respectively) was different than our classification, which could explain the larger concentrations. Also the study in Helsinki was developed in the summer while ours represents an average of all seasons.

3.3 Seasonal variations of ions and particles

The number concentrations of small ions of both polarities (Fig. 3a) were the highest in the summer and autumn (maxima between July and September, depending on the polarity, Fig. A4) and lowest in the spring. Concentrations in January and February were also relatively high. Lopez et al. (2012) measured concentrations of ^{222}Rn for eight years in Gif-sur-Yvette, 20 km away from the LHVP site, and reported the highest radon concentrations in autumn and the lowest in the summer/spring. As radon and gamma radiation are major sources of small ions in continental areas (Hirsikko et al., 2011), the seasonality of small ions is partially associated to the seasonality of radon exhalation, which depends for instance on boundary layer mixing height, presence of fog, snow coverage and soil humidity (Lopez et al., 2012). Despite the differences in altitude, Rose et al. (2013) also observed the lowest concentrations of small ions in spring in Puy de Dôme, a mountain in central France (1465 m a.s.l.). In Athens, the highest concentrations of small ions were observed in the summer (Retalis et al., 2009). As radon emissions depend on several factors, concentrations of small ions are expected to vary among sites. In addition to radon concentrations, in spring the higher frequency of NPF may also have increased the scavenging of small ions.

The median number concentrations of positive intermediate ions (Fig. 3b) varied with season showing the highest median number concentrations in spring, whereas the median number concentrations of the negative intermediate ions were lower ($< 10\,cm^{-3}$) and more stable throughout the year. For positive intermediate ions, the highest monthly median concentrations were observed in February, March and May (peak), while for the negative polarity, the highest were observed in February, March (peak) and November (Fig. A4). The concentrations of positive intermediate ions were highly variable in July (Fig. A4), with 75th percentile reaching nearly $200\,cm^{-3}$. Because intermediate ions are mostly observed during NPF events (Tammet et al., 2014) and these events occur more often in the spring/summer (Manninen et al., 2010), high number concentrations of intermediate ions during these seasons were expected. In general, the results suggest that positive intermediate ions were more affected by seasonality than the negative intermediate ions.

The number concentrations of positive large ions were also fairly stable throughout the seasons (between 400–450 cm^{-3}), whereas the number concentrations of negative large ions were less stable (between 230 and 310 cm^{-3}) showing lowest in the summer and highest in the winter and autumn (Fig. 3c), resembling the seasonal variations of particle number (Fig. 3d). Aalto et al. (2005) showed that in several European cities particle number concentrations were highest in the winter and lowest in the summer, in agreement with our study. Pikridas et al. (2015), also reported this pattern for Paris and surrounding areas. The lower mixing height of the boundary layer and the need for heating are possible drivers for the increase in particle number concentrations in the winter.

3.4 Frequency of NPF events

To analyse new particle formation events we classified days into NPF event, NPF non-event and undefined as described in Hirsikko et al. (2007a). The monthly frequency of

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NPF events in LHVP is shown in Fig. 4 as percentage of NPF events per number of days. On average, NPF events occurred between February and October, being most frequent in the spring and summer (highest in May and July) and least frequent in the winter. Undefined and NPF non-event days on the other hand occurred throughout the year. Manninen et al. (2010) analysed NPF based on ion concentrations in twelve European sites and reported that several sites showed highest frequency of NPF event days in spring/summer and minimum in the winter, in agreement with our study. Studies from urban areas such as Helsinki, Budapest, Beijing and Pittsburgh also reported high incidence of NPF in spring (Salma et al., 2011; Hussein et al., 2008; Wu et al., 2007; Stanier et al., 2004). Pikridas et al. (2015) also observed considerably higher frequency of NPF events in the summer than in the winter in Paris and in two surrounding suburban sites.

The higher incidence of solar radiation favours photochemical reactions in the atmosphere in spring and summer which may consequently increase the frequency of NPF, as observed by Pikridas et al. (2015). In addition to meteorological conditions, the air in LHVP and in several other sites in Europe is cleaner in the summer than in the winter (Aalto et al., 2005; Pikridas et al., 2015). Thus, NPF was likely favoured by fewer aerosol particles acting as condensation sinks (Salma et al., 2011; Wu et al., 2007; Stanier et al., 2004; Pikridas et al., 2015) in the summer.

In our study air ions were monitored for a total of 442 days, out of which 57 days were NPF events (about 13 %), 94 were undefined days and 291 were NPF non-event days. In non-urban environments, NPF was observed to occur somewhere between 21 and 57 % of the days depending on the site (Manninen et al., 2010). In urban areas, however, NPF is expected to be less frequent due to the higher number of condensation sinks competing for condensing vapours (Hussein et al., 2008). In cities such as Nanjing (China), São Paulo (Brazil), Helsinki (Finland), Shanghai (China), Pune and Kanpur (India), Birmingham (UK) and Budapest (Hungary) the frequency of NPF events was between 5–27 % (Herrmann et al., 2014; Backman et al., 2012; Hussein et al., 2008; Du et al., 2012; Kanawade et al., 2014; Zhang et al., 2004; Salma et al., 2011) which is

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within range of the observations in Paris (13 %). However, NPF frequencies as high as 40–55 % were observed in Beijing, Pittsburgh and Brisbane (Wu et al., 2007; Stanier et al., 2004; Crilley et al., 2014), although not all the studies comprised an entire year of measurements.

3.5 Diurnal cycle of ions during new particle formation

Figure 5 shows the differences in diurnal cycles of ions and particles on NPF events and NPF non-event days. In this section, only strong NPF events were considered (21 NPF event days). On NPF event days, a clear peak was observed between 09:00 and 11:00 (UTC) for intermediate ions and at 12:00–14:00 for large ions and particle number, whereas on NPF non-event days these "noon" peaks were completely absent. As NPF is often observed at noon, an increase in concentrations around this time was expected. The time-lag in peak concentrations was likely caused by growth of intermediate ions. During NPF, the highest increase in concentrations occurred for intermediate ions, with median maxima of 50–80 cm^{-3} (10:00–11:00), about 8.5–10 times higher than on the same hour of NPF non-event days, depending on the polarity. Because the median concentrations of intermediate ions were very low on NPF non-event days ($< 12\,cm^{-3}$), the results suggest that intermediate ion concentrations may be used as indicator for NPF events in Paris. The median particle number and large ion concentrations increased 1.2 times (12:00) and 1.5–1.8 times (12:00–13:00), respectively, on NPF event days in comparison to the same hour on NPF non-event days. Thus, despite its relatively low frequency (13 %), NPF was an important source for intermediate ions, large ions and particles in Paris around noon. The increase in particle number during NPF days contributes to climatic effects and deterioration of the urban air quality. In cities such as Pittsburgh, USA, where the frequency of NPF events is high (50 %) (Stanier et al., 2004), particle number concentrations roughly doubled during NPF bursts (45 000 cm^{-3}) in comparison to the morning rush hours of workdays (23 000 cm^{-3}). The authors estimate that the particle number daily averages on NPF event days was about 40 % higher than on NPF non-event days. In LHVP, the mean of

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the daily mean concentrations on event days (11 744 cm^{-3}) was in fact lower than on NPF non-event days (14 259 cm^{-3}) probably due to the lower concentrations of aerosol particles in the mornings of NPF event days.

As mentioned, in the morning of event days the concentrations of large ions and especially aerosol particles (Fig. 5e–g) were lower than on NPF non-event days, which may have favoured NPF. This result is consistent with the idea that NPF can be favoured on weekends due to the lower load of condensation sinks. The cleaner atmospheric conditions illustrated in Fig. 5 could have been caused for instance by enhanced turbulent vertical mixing on NPF days (Nilsson et al., 2001). According to Wehner et al. (2010) and Nilsson et al. (2001) a higher vertical mixing could favour NPF not only by increasing the dilution of condensation sinks into the atmosphere, but also by mixing condensable vapours with cooler air from higher altitudes, thus increasing supersaturation, or even by transporting clusters formed at higher altitudes downwards.

New particle formation did not affect the small ion concentrations as much as it did the other particle sizes. On event days, the concentrations of positive small ions decreased roughly around noon in comparison to NPF non-event days, indicating scavenging of these ions by the newly formed particles. This decrease around noon was also observed for negative small ions, however, the number concentrations of these ions were in general slightly lower on NPF event days in comparison to NPF non-event days. Winkler et al. (2008) indicates that ion-induced nucleation is formed preferably onto negative ions, thus, the decrease in negative small ion concentrations could indicate that part of these ions were used during ion-induced nucleation. Yet, we only observed a weak positive correlation (r = 0.10 to 0.25, $p < 0.01$) between intermediate and small ions (Fig. A5). In general, no clear correlation between NPF (intermediate ion/small ions) and small ions or particle number was observed (Fig. A6).

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4 Case study of four NPF event days

We selected four NPF event days of various intensities and duration to observe the behaviour of ions and aerosol particles during the bursts (Fig. 6). In all the four days, a "banana" shaped NPF event was observed. This type of NPF event is likely of regional nature as it requires uniform air masses to last for at least a few hours (Manninen et al., 2010). Thus, the gaps in the "bananas" (Fig. 6b and c) could be caused by some degree of heterogeneity in the regional air masses. According to Hussein et al. (2009), regional NPF events may spread for over 200 km and the newly formed particles may be traced for as long as 30 h before they merge into background levels. Pikridas et al. (2015) analysed NPF events in LHVP and in two suburban sites near Paris, GOLF and SIRTA (20 km NE and 20 km SE from Paris, respectively). The authors measured particle number size distributions in all the three sites during the summer of 2009 and winter 2010. The results showed that nearly all the NPF events observed in SIRTA in the summer were also observed in LHVP, and roughly half of these events (6 event days) were also observed at GOLF, thus covering at least 40 km in extension. The results by Pikridas et al. (2015) indicate that at least half of the NPF events observed in LHVP in the summer were regional in nature.

The diurnal behaviour of ions varied considerably among the four days. In most of the examples, NPF started between 08:00 and 12:00 (UTC). A "pool" of small ions was observed in all the four days suggesting the constant presence of these ions, in agreement with previous studies (Manninen et al., 2009). No significant changes in small ion number concentrations were observed during the bursts (Fig. 6e–h). The number concentrations of intermediate ions (both polarities) however increased 4–15 times (depending on the day) during the bursts in comparison to the number concentrations immediately before the bursts, reaching mean values as high as 420 cm^{-3} (positive polarity) on the 31 March 2010. For large ions the concentrations were 1.8–6 times higher during the bursts, and for particle number concentrations it was 1.3–2 times higher (depending on the day). On the 19 May 2010, particle number reached

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28 600 cm^{-3} during the NPF burst (13:00), a value considerably higher than the mean concentrations observed in the morning rush hours of workdays (Fig. 2g: 19 500 cm^{-3}, 08:00). Once again, during the NPF events the concentrations of large ions and particle number peaked about 1 h later than that of intermediate ions, indicating growth. Hence, the results confirm that NPF events can considerably increase the number concentration of intermediate ions (2–7 nm), large ions (7–20 nm) and aerosol particles in the urban air.

Crippa et al. (2013) analysed the composition of aerosol particles during the winter in LHVP and reported that PM_1 particles (particulate matter, dp < 1 µm) were composed of organics (33 %), nitrates (28.1 %), sulphates (15.9 %), ammonium (13.6 %), chlorine (1.0 %) and BC (8.3 %). Organic vapours (Kulmala et al., 2013), ammonium and sulphates precursors (Crilley et al., 2014) were associated to NPF and growth of particles and thus may have aided the NPF events in LHVP.

5 Growth rates of ions

Particles growth rate (GR) is proportional to the concentrations of condensing vapours in the air. We calculated GR for ions in diameter of 1.9–3; 3–7 and 7–20 nm. A total of 21 strong NPF events were used in the calculations, 9 of which were workdays and 12 were weekends. Thus, the results once again suggest that NPF (in this case strong NPF events) may be favoured on weekends due to the lower load of condensation sinks. In general, the GR of ions (Table 2) increased with ion size (median: 1.9–3 nm: 3.4 nm h^{-1}; 3–7 nm: 5.9 nm h^{-1}; 7–20 nm: 6.9 nm h^{-1}) in agreement with previous studies, including urban areas (Yli-Juuti et al., 2011; Manninen et al., 2010; Kulmala et al., 2012, 2004b; Backman et al., 2012; Herrmann et al., 2014). The results support the theory that condensing vapours aiding the growth of ions from 3–20 nm may differ in composition from vapours aiding the growth of smaller ions, as suggested by previous studies (Manninen et al., 2010). In addition to different chemical composition, Kulmala et al. (2004b) suggests that the increase in GR with particle size could also relate to the diurnal availability of condensing vapours and Nano–Köhler effect (Kulmala et al., 2004a). If the diurnal peak in vapour concentration occurred after NPF, there would be less vapours available to grow the smaller particles in comparison to the larger ones (growing later). The Kelvin effect (Kulmala et al., 2004a, b; Yli-Juuti et al., 2011) and the Nano–Köhler effect (Kulmala et al., 2004a) may also influence the GR as they favour evaporation of small particles and growth of larger ones. Moreover, the median GR was higher on workdays than on weekends for ions from 3–7 and 7–20 nm. This pattern was not as evident for ions from 1.9–3 nm nor for mean GR values.

The GR of ions from 3–20 nm were higher on workdays likely due to the higher availability of traffic-emitted condensable vapours. In cities such as São Paulo, Nanjing and Helsinki, the reported mean GR for ions were 2.1–5.3, 6.3–9.7 and 8.0–11.4 nm h^{-1} for size ranges of 1–3, 3–7 and 7–20 nm (7–30 nm in Nanjing), respectively, and were in range with the GR observed in the LHVP site (Table 2). Manninen et al. (2010) reported median GR of ions in European sites (mostly rural and coastal sites) to be 2.8 nm h^{-1} for particles of 1.5–3 nm; 4.3 nm h^{-1} for particles of 7–20 nm, and 5.4 nm h^{-1} for particles of 7–20 nm, which are mostly lower than the values observed in the urban areas. Hussein et al. (2008) compared NPF characteristics between Helsinki and Hyytiälä, a rural area in Finland. The authors observed higher GR in Helsinki and concluded that the higher availability of condensing vapours and the large number of aerosol particles in Helsinki probably enhanced growth by condensation and coagulation in comparison to Hyytiälä. Note that, as Hussein et al. (2008) and Yli-Juuti et al. (2011) pointed out, the GR calculation method is somewhat subjective and thus also influences GR values. Moreover, GR can also vary among instruments (Yli-Juuti et al., 2011).

The median CS concentrations were only slightly higher on workdays in comparison to weekends (Table 2) indicating that part of the particle surface area may also originate from long range transport. Sciare et al. (2010) analysed the composition of $PM_{2.5}$ in Paris and reported that the city receives polluted air masses ($PM_{2.5}$) from North-Western and Central Europe. Note that CS calculations were based on roughly two months of data, and thus are not representatives for the entire campaign.

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6 Summary and conclusions

Atmospheric ion number size distributions (0.8–42 nm) were measured in an urban background site of Paris, France, using an Air Ion Spectrometer (AIS) from 26 June 2009 to 4 October 2010. Aerosol particles were counted simultaneously using a combination of TDMPS (6–740 nm) and CPC (> 6 nm). The ions were size segregated as small or clusters (0.8–2 nm), intermediate (2–7 nm) and large ions (7–20 nm). We analysed frequency and seasonal variations of NPF events, diurnal and seasonal cycles of ions and aerosol particles, as well as the behaviour of ions and their growth rates during NPF events. Condensation sinks were also calculated.

On workdays, particle number concentrations peaked in the mornings and evenings, reflecting the traffic rush hours. During the morning peak, the concentrations of small and intermediate ions decreased whereas the concentrations of large ions increased. This indicates that aerosol particles from traffic acted as scavengers for small and intermediate ions. Both ions and aerosol particle concentrations varied with season, and these variations differed with ion polarities. Number concentrations of small ions were lowest in the spring, when number concentrations of positive intermediate ions were highest. The results thus indicate that when comparing ion concentrations from different studies, one should consider the season in which the study was developed and also the polarity regarded.

New particle formation was present on 13 % of the days (34 weekdays and 23 weekends), which is a low frequency compared to cleaner sites but is in range with the reported in several other busy cities. Seasonally, NPF occurred mainly in late the spring and summer, and were completely absent from November to January. Undefined days, however, occurred throughout the year. Higher frequency of photochemical reactions along with lower number concentrations of aerosol particles may have enhanced the frequency of NPF in the summer. The growth rates of ions during NPF events increased with ion size and had median values varying between 3–7 $nm\,h^{-1}$ in Paris. Previous studies suggest the Kelvin and the Nano–Köhler effects (Kulmala et al., 2004a) as well as the diurnal cycle and composition of condensing vapours as possible factors influencing the growth pattern. Moreover, the median growth rates of ions were higher on workdays than on weekends for ions from 3 to 20 nm, but this pattern was unclear for ions from 1.9 to 3 nm and for mean GR values. A higher GR during workdays suggests higher availability of condensing vapours in comparison to weekends.

The diurnal cycle of ions and particles during NPF events and NPF non-event days suggest that NPF was an important contributor for both ions and aerosol particles in Paris. On average, the NPF bursts caused an extra peak between 09:00 and 14:00 in the diurnal cycles of intermediate ions, large ions and particle number. The intermediate ions were by far the most affected by NPF, with median concentrations increasing 8.5 to 10 times during the bursts in comparison to the same hour on NPF non-event days. Because the median number concentrations of intermediate ions were so low on NPF non-event days ($< 12\,\mathrm{cm^{-3}}$) in comparison to NPF event days (50–$80\,\mathrm{cm^{-3}}$), the results suggest that intermediate ion number concentrations could be used as an indicator for NPF in Paris. The intermediate ions produced during the bursts grew to larger sizes on average within a few hours, increasing the median number concentrations of large ions and aerosol particles by a factor of 1.5–1.8 (depending on the polarity) and 1.2, respectively, in comparison to NPF non-event days. The diurnal cycles also showed that on average the particle number concentrations were lower in the morning of NPF event days in comparison to NPF non-event days, and that concentrations of intermediate ions were higher in the mornings of weekends in comparison to workdays. These results indicate that NPF in Paris was favoured on weekends, when the load of aerosol particles was lower. This idea was reinforced by the statistics of strong NPF events. Out of the 21 strong NPF events, 9 were observed on workdays and 12 were on weekends.

In general, as aerosol particles are associated to adverse health effects, the results suggest that NPF events influenced the air quality in Paris around noon, especially during the spring and summer, when the frequency of NPF was highest.

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Table 1. Statistical summary of particle number concentration (6–740 nm) and small (0.8–2 nm), intermediate (2–7 nm) and large ion (7–20 nm) number concentrations in Paris for the entire campaign. Total ions represent ions in the size range of 0.8–42 nm in size. Concentrations were presented as particles cm^{-3} and were based on 1 h means.

	Mean	Std	5 %	25 %	50 %	75 %	95 %	No. of hours (1h scale)
Small ions (+)	330	150	130	230	310	400	600	7810
Small ions (-)	390	180	160	270	360	470	740	7820
Intermediate ions (+)	30	40	0	0	10	30	100	10 310
Intermediate ions (-)	20	70	0	0	10	10	60	10 310
Large ions (+)	460	240	160	290	410	590	910	10 310
Large ion (-)	310	180	80	180	270	410	650	10 310
Total ions (+)	1640	660	780	1180	1530	1980	2880	10 310
Total ions (-)	1270	540	590	900	1180	1530	2290	10 310
Particle number concentration[a]	13 690	6430	5590	9200	12 460	16 840	26 000	9310
CS[b] $_{(3–740\,nm)}$ ($\times 10^{-3}\,s^{-1}$)	14.3	8.4	4.7	7.9	12.7	18.1	31.3	1520

[a] Particle number: combined TDMPS (6–740 nm; 29 June 2009–31 July 2009) and CPC (dp_{50}: 6 nm; 11 August 2010–4 October 2010) measurements.
[b] CS was calculated based on the TDMPS size distribution from 29 June 2009–31 July 2009 and 15 January 2010–19 February 2010.

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Table 2. Growth rates of ions (mean of positive and negative) calculated from 21 NPF event days (9 workdays and 12 weekends). The total growth rates (GR_{tot}) include both workdays and weekends. The unit for GR is nm h^{-1}. The CS calculations were based on TDMPS data from July 2009 and January/February 2010 (hourly means).

	Mean	5 %	25 %	50 %	75 %	95 %	No. of days
GR_{tot} (1.9–3 nm)	4.0	1.3	2.5	3.4	5.7	7.4	21
GR_{tot} (3–7 nm)	7.6	1.9	3.9	5.9	9.1	24.1	21
GR_{tot} (7–20 nm)	8.5	4.0	6.3	6.9	10.8	17.6	21
Workdays							
GR (1.9–3 nm)	4.1	2.1	2.8	3.4	5.7	6.9	12
GR (3–7 nm)	7.1	3.1	4.4	6.8	9.3	12.2	12
GR (7–20 nm)	8.8	6.4	6.8	8.0	9.1	16.5	12
$CS_{(3-740\,nm)}$ ($\times 10^{-3}\,s^{-1}$)	14.9	5.2	8.5	13.1	18.5	33.2	51
Weekends							
GR (1.9–3 nm)	3.9	1.0	2.1	3.3	5.5	7.9	9
GR (3–7 nm)	8.0	1.7	3.2	5.0	8.4	28.4	9
GR (7–20 nm)	8.3	3.6	4.5	6.5	11.6	18.6	9
$CS_{(3-740\,nm)}$ ($\times 10^{-3}\,s^{-1}$)	12.7	3.7	7.1	11.1	16.7	26.7	19

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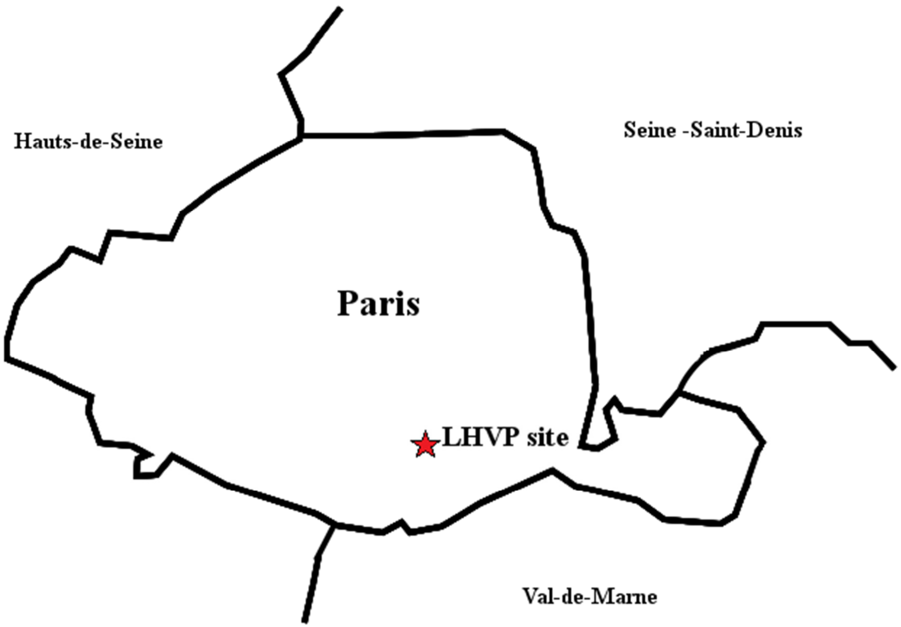

Figure 1. Location of the LHVP site in Paris.

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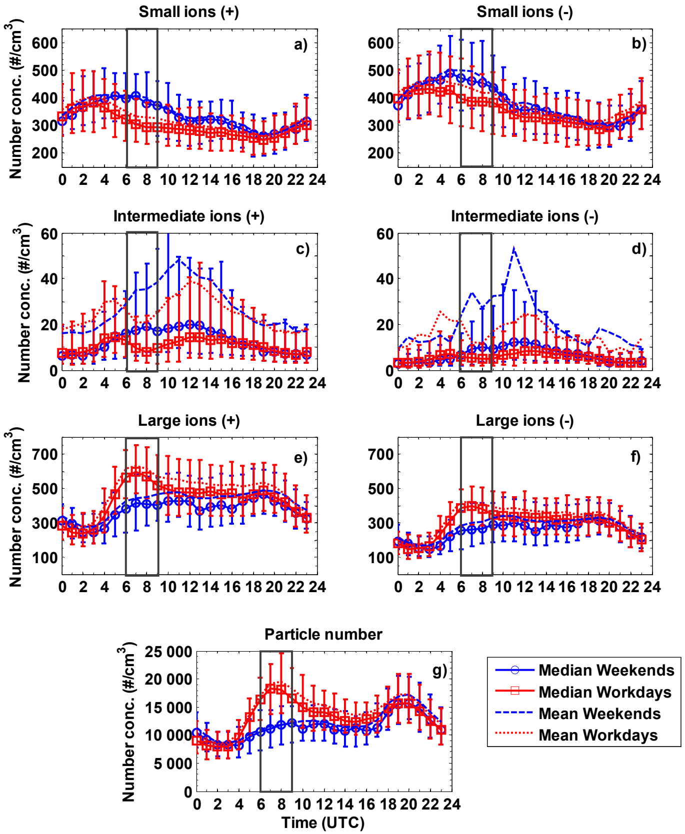

Figure 2. Diurnal cycle of particle number concentrations (> 6 nm) **(g)**, and small (0.8–2 nm), intermediate (2–7 nm) and large ions (7–20 nm) **(a–f)** for workdays and weekends. The markers show the hourly median concentrations and the whiskers show 25th and 75th percentiles. The dashed lines represent mean concentrations, and the rectangles (06:00–09:00) indicate the morning peak of particle number.

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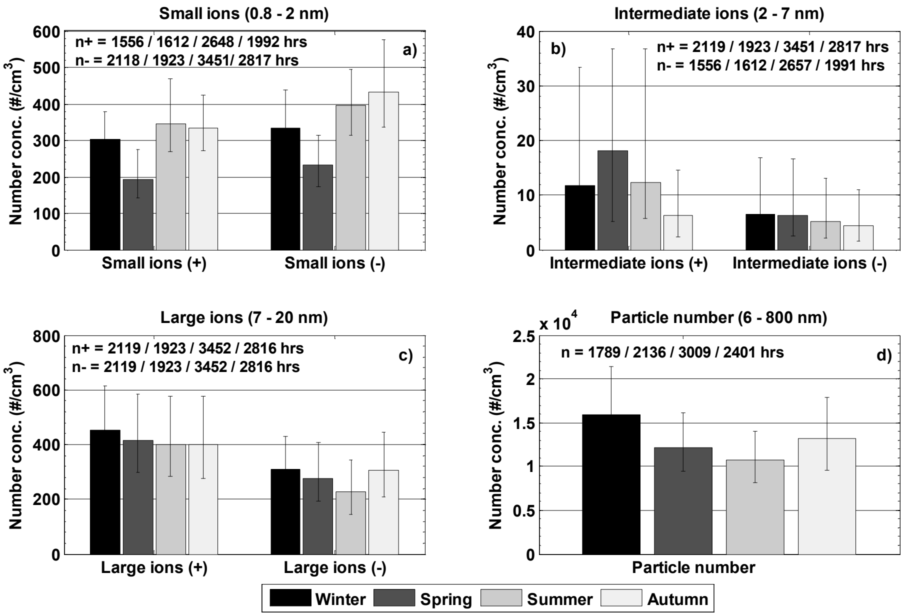

Figure 3. Seasonal variations of particle number **(d)** and positive/negative ions **(a–c)**. The bars represent median concentrations, the whiskers represent 25th and 75th percentiles, and n (±) represents the number of hours included in each season (winter/spring/summer/autumn).

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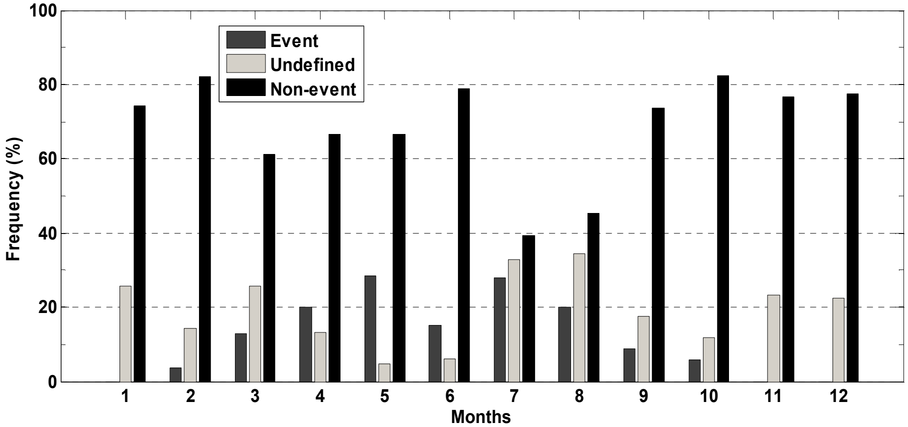

Figure 4. Monthly frequency (%) of NPF events, NPF non-events and undefined days. Data collected continuously from July 2009 to September 2010.

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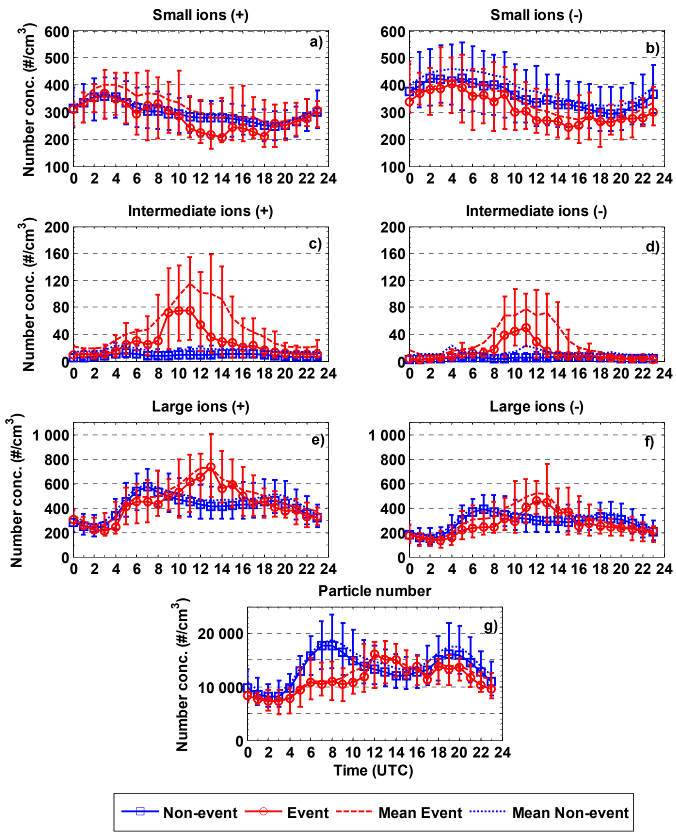

Figure 5. Diurnal cycle of aerosol particles and ions (small: 0.8–2 nm; intermediate: 2–7 nm; large: 7–20 nm) on strong NPF event days and NPF non-event days. The markers show the hourly median number concentrations and the whiskers show 25th and 75th percentiles (1 h data points).

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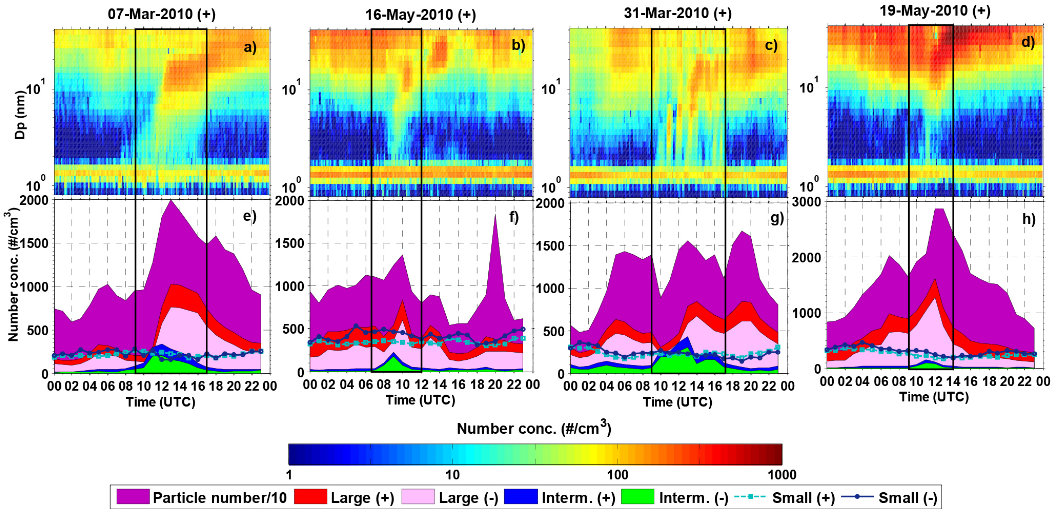

Figure 6. Examples of NPF event days observed in the LHVP site. The first row of figures represent positive ions measured using AIS (dp: 0.8–42 nm) with a time resolution of 3 min. The second row represents mean number concentrations of particle total number (> 6 nm), small (0.8–2 nm), intermediate (2–7 nm) and large ions (7–20 nm), at a resolution of 1 h. Note that absolute particle number concentration is obtained by multiplying the concentrations by 10. The black rectangles indicate the NPF bursts.

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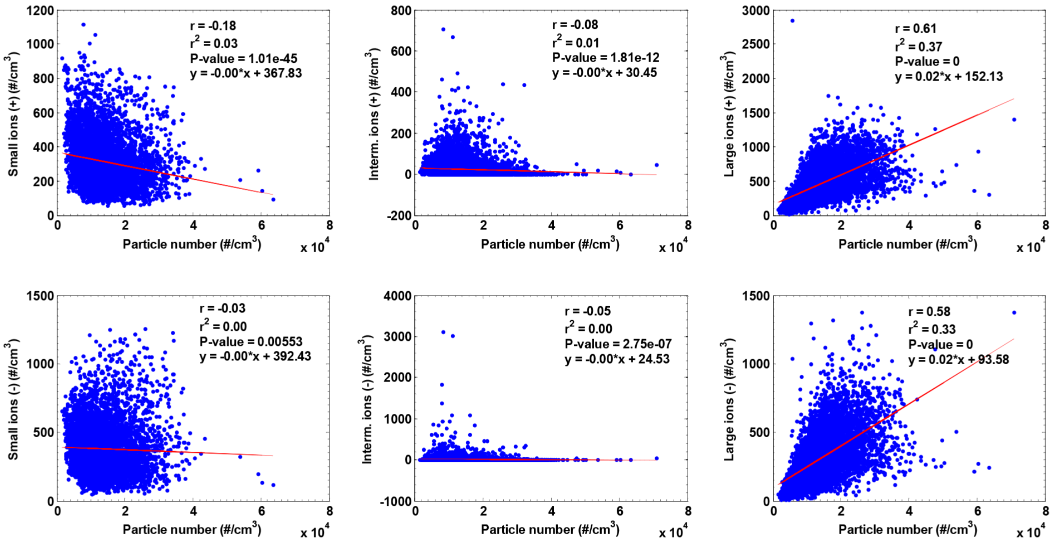

Figure A1. Correlation between particle number concentrations and ions (small: 0.8–2 nm; intermediate: 2–7 nm; large: 7–20 nm).

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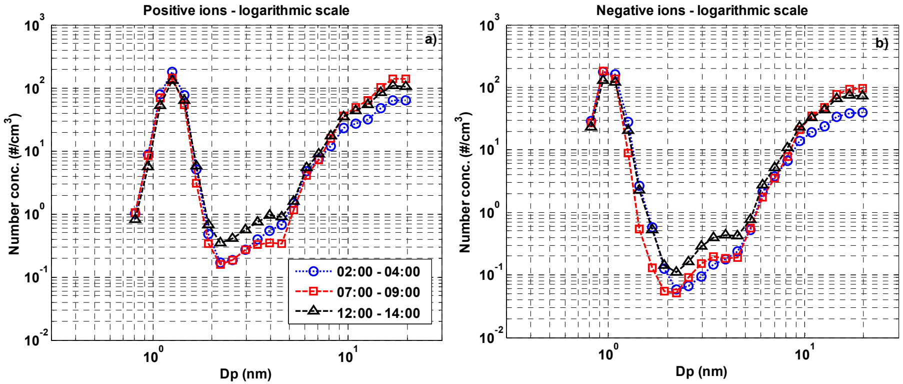

Figure A2. Median size distribution of ions on workdays: early morning (02:00–04:00), rush hours (07:00– 09:00) and noon (12:00–14:00).

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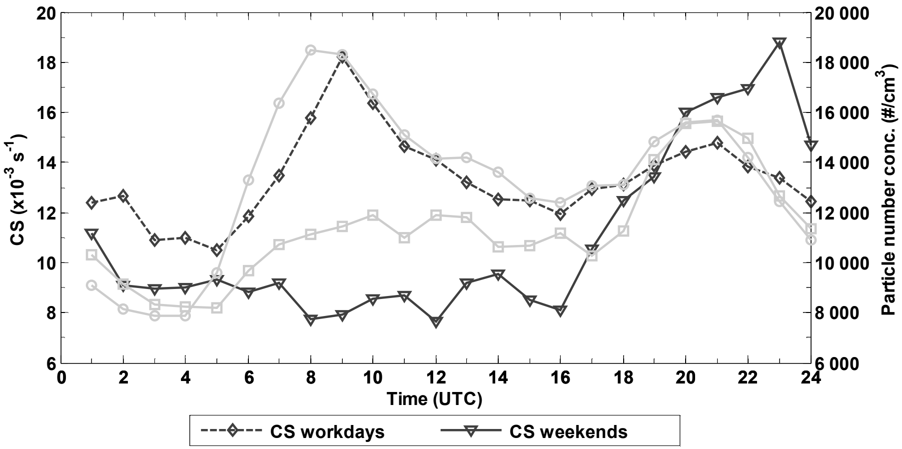

Figure A3. Diurnal cycle of condensation sink (CS) based on data from 1–31 July 2009 and 15 January–15 February 2010 (1 h resolution) and particle number concentrations. The markers represent median of hourly means.

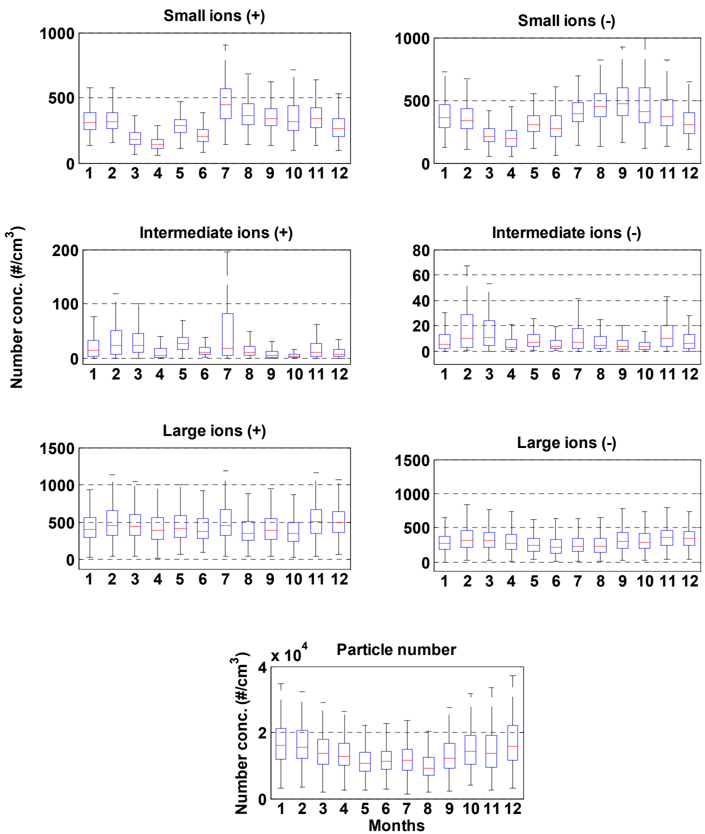

Figure A4. Monthly variations of ions and particles in Paris. The edges of the boxes represent 25th and 75th percentiles, the central line is the median, the whiskers represent the highest concentrations (not considered outliers). The data comprise of the period 1 July 2009–30 September 2010.

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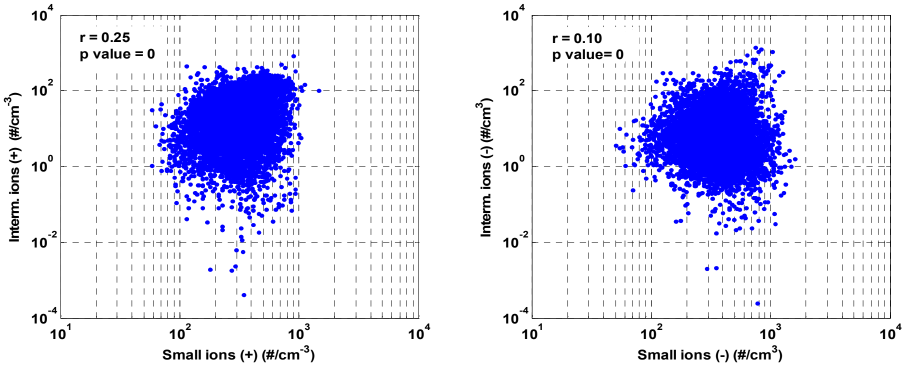

Figure A5. Correlation between intermediate ions and small ions.

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Variability of air ion concentrations in urban Paris

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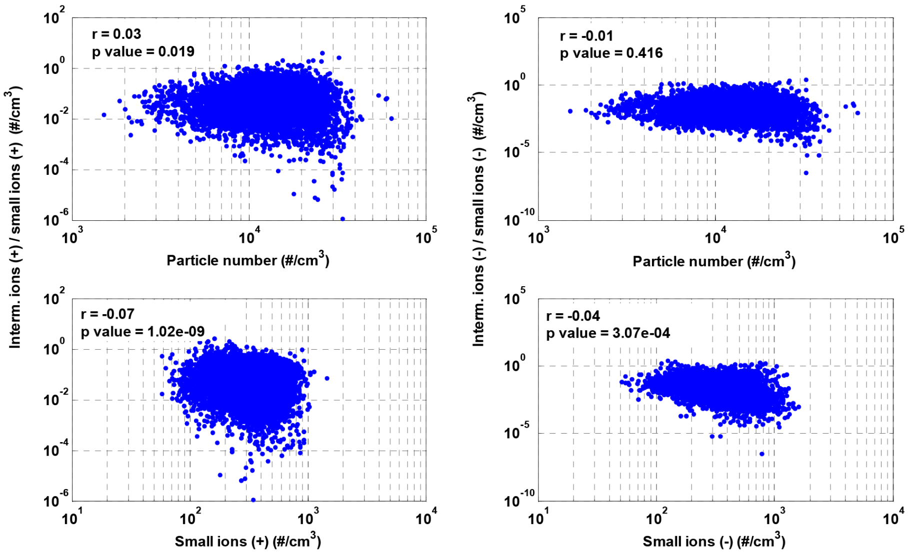

Figure A6. Correlation between the ratio intermediate ions/small ions and particle number and small ions.

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