Size-dependent particle activation properties in fog during the ParisFog 2012/13 field campaign

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Abstract. Fog induced visibility reduction is responsible for a variety of hazards in the transport sector. Therefore there is a large demand for an improved understanding of fog formation and thus improved forecasts. Improved fog forecasts require a better understanding of the numerous complex mechanisms during the fog life cycle. During winter 2012/13 a field campaign called ParisFog aiming at fog research took place at SIRTA (Instrumented Site for Atmospheric Remote Sensing Research). SIRTA is located about 20 km southwest of the Paris city centre, France, in a semi-urban environment. In situ activation properties of the prevailing fog were investigated by measuring: (1) total and interstitial (non-activated) dry particle number size distributions behind two different inlet systems; (2) interstitial hydrated aerosol and fog droplet size distributions at ambient conditions; (3) cloud condensation nuclei (CCN) number concentration at different supersaturations (SS) with a CCN counter. The aerosol particles were characterized regarding their hygroscopic properties, fog droplet activation behaviour and contribution to light scattering for 17 developed fog events. Low particle hygroscopicity with an overall median of hygroscopicity parameter, \( \kappa \), of 0.14 was found, likely caused by substantial influence from local traffic and wood burning emissions. Measurements of the aerosol size distribution at ambient RH revealed that the critical wet diameter, above which the hydrated aerosols activate to form droplets, is rather large with a median value of 2.6 \( \mu m \) and is highly variable (ranging from 1 to 5 \( \mu m \)) between the different fog events. Thus, the number of activated fog droplets was very small and the non-activated hydrated particles were found to contribute significantly to the observed light scattering and thus to the reduction in visibility. Combining all experimental data, the effective peak supersaturation, \( SS_{peak} \), a measure of the peak supersaturation during the fog formation, was determined. The median \( SS_{peak} \) value was estimated to be in the range from 0.031 to 0.046 % (upper and lower limit estimations), which is in good agreement with previous experimental and modelling studies of fog.

1 Introduction

Aerosol hygroscopicity is defined as the ability of aerosol particles to take up water. This water uptake plays an important role in the Earth’s radiative budget as it changes the particle’s light scattering and absorption properties. The interaction of aerosol with solar radiation can either be direct, or through the aerosol’s modification of cloud properties. Aerosols influencing fog are also a major factor in visibility reduction at surface levels, which can cause fatalities in traffic (Rosenfeld, 1996). When the relative humidity increases, particles can grow substantially and if the atmosphere becomes supersaturated with respect to water vapor, particles can activate to form fog droplets (e.g., [Bergot, 2007], depending on their size and hygroscopic properties. The term mist is used if visibility drops below 5 km (Vautard et al.)
is at their SS crit particles can grow to while still being in stable equilibrium, activated in the hydrated aerosol mode. The largest size that the peak supersaturation of the air parcel will remain non-

Those particles having a larger critical supersaturation than aerosol-to-cloud droplet activation and is thus an important extinction (sum of scattering and absorption) of visible radi-

uum size by taking up water, remaining smaller than acti-

vated droplets, but large enough to contribute significantly to extinction (sum of scattering and absorption) of visible radiation in fog (Elias et al. 2009).

Despite the advances in modelling (e.g., Bott et al. 1990; Stolaki et al. 2012), the representation of the physical processes leading to fog formation has not yet progressed to the point where numerical models can accurately forecast/nowcast fog events (Gultepe et al. 2007). The goals of this study are to examine the interaction between particles and fog, and the partitioning of water within this system to improve the understanding of fog formation.

A detailed examination of the aerosol properties during fog occurrence was performed to determine which fraction of the total particles is activated to fog droplets (Sect. 4.1). The activation properties of the particles within fog are further investigated by comparing dry with ambient (humid) size distribution measurements. The effective peak supersaturation is quantified and discussed for the fog events observed at the SIRTA site (Sect. 4.2). The contribution of hydrated but non-activated particles to the visibility reduction during fog is also investigated and the relative contribution of stable non-activated particles and activated particles to the light scattering is presented (Sect. 4.3).

2 Experimental

2.1 ParisFog 2012/13 campaign

ParisFog is a series of field campaigns focusing on fog research (Haefelin et al. 2010). They have taken place at the Instrumented Site for Atmospheric Remote Sensing Research (SIRTA) several times since 2006. SIRTA is located in the immediate vicinity of the Ecole Polytechnique Palaiseau, on the Saclay plateau about 20 km southwest of Paris city centre. The site is located in a semi-urban environment composed of roughly equal portions of agricultural fields, wooded areas, housing and industrial developments (Haefelin et al. 2005). SIRTA hosts active and passive remote sensing instruments to continuously quantify cloud and particle properties, as well as key atmospheric parameters (Haefelin et al. 2005). During the ParisFog 2012/13 campaign in the winter season (October to March), additional measurement instruments were provided and operated by several research institutes, as described below. During this time, the goal was to closely observe surface conditions, large- and small-scale dynamics, radiation, turbulence, precipitation, droplet- and particle-microphysics and -chemistry. The data presented in this study covers the time period from 2 October 2012 to 7 January 2013.

2.2 Instrumentation

The instrumentation used in this study is listed in Table 1. For the sampling of the particles and hydrometeors, a total and an interstitial inlet were installed on the roof of a measurement container at 4 meters above ground level. The total inlet collected all particles (including droplets). The water associated with the hydrometeors and aerosol particles was evaporated
by heating the top part of this inlet to approximately 20 °C, and subsequently all dried aerosol particles (non-activated aerosols and the residuals of the fog droplets) reached the instruments in the laboratory. The interstitial inlet sampled particles with an aerodynamic diameter smaller than 1 µm at ambient RH (from 17 October 2012 07:00 to 14 November 2012 16:00 UTC). In the laboratory, the aerosol from both the interstitial and total inlets was dried to RH<20% as it was heated to room temperature (typically 20 to 30 °C). The maximum diameter of the sampled aerosol particles was increased to 2 µm from 2 October 2012 17:00 to 17 October 2012 07:00 UTC and from 14 November 2012 16:00 to 7 January 2013 15:00 UTC. The cut-off diameter of the interstitial inlet was varied, in order to test how the best separation between interstitial particles and activated fog droplets could be achieved. This inlet consists of an aerodynamic size discriminator (PM2.5+, Very Sharp Cut Cyclone, BGI, USA and PM1, Sharp Cut Cyclone 2.229, BGI Inc.) running at flow rates of ~20 lpm (PM2.5) or ~16 lpm (PM1). The term interstitial is based on the assumption that all particles larger than the applied cut-off consist of activated cloud droplets.

However, this was not always the case, particularly when the smaller cut-off diameter of 1 µm was applied, as discussed in Sect. 4.2.

Inside the container the dried number size distributions of total and interstitial particles were measured with a scanning mobility particle sizer (SMPS) consisting of a differential mobility analyser (DMA; TSI 3071) and a condensation particle counter (TSI CPC 3022). The DMA was operated at a sample air flow rate of 0.3 lpm and a closed loop excess and sheath air setup with a flow rate of 3 lpm. The measured mobility diameters ranged from 13 nm to 520 nm. The scan time of one size distribution was 6 min and after each scan the instrument was automatically switched between the total and interstitial inlets. The mean size distributions measured behind either inlet agreed well during fog-free periods as both inlets deliver the total aerosol under these conditions. However, the total number concentration differed by up to 15 % between consecutive scans due temporal variability of aerosol concentration. To minimize the effects of aerosol variability on the calculated activation curves, the total size distribution was compared with the average of the two interstitial size distributions measured immediately before and after.

To measure the cloud condensation nuclei (CCN) number concentration, a miniature continuous flow streamwise thermal gradient CCN chamber (m-CCNC; Sullivan et al., 2009) was installed downstream of the total inlet. This instrument was constructed at Scripps Institution of Oceanography based on the design of Roberts and Nenes (2005). The particles sampled behind the total inlet are introduced to the centre of a column surrounded by a sheath of filtered humidified air. A linear temperature gradient along the column produces a well-defined and controlled supersaturation (SS) with respect to water. The SS is defined by the temperature gradient and the flow rate. Particles that take up water and grow to a diameter size of > 1 µm are detected by an optical particle counter at the end of the column and are counted as CCN. The temperature differences and flow rate were scanned from 4 to 14 K and from 0.1 to 0.28 lpm, respectively, such that a SS range of 0.05 to 0.6 % was achieved (for the uncertainties, see Table [1]). The m-CCNC was calibrated before and after the campaign using monodisperse ammonium sulphate particles (nebulized from a solution, dried by a diffusion drier and size segregated by a DMA).

For the data analysis it is important to know when fog was present and especially how dense it was. For this task a Degreanne forward scatter sensor DF20+ was operated at a height of 3 m above the ground. The instrument provided a measurement of the horizontal visibility with a white light source (wavelength from 350 to 900 nm) and a receiver placed off axis from the source. In addition, a Particle Volume Monitor (PVM-100; Gerber [1991]) additionally measured the liquid water content (LWC\textsubscript{PVM}) by forward light scattering.

An optical particle counter, WELAS 2000 (Palas Inc.), was used to measure the number size distribution of hydrosol aerosol particles and fog droplets up to a diameter of ~10 µm at ambient conditions by means of light scattering (size range between 360 nm and 42 µm water droplet equivalent diameter). Droplets larger than ~10 µm could not be measured due to the inlet used with the WELAS 2000 (Burnet et al., 2012; Elias et al., 2014). The instrument was calibrated in the laboratory with monodisperse latex spheres (PSL; index of refraction = 1.59). During fog events, when the RH is ~100%, the particles can be expected to be hydrated and mainly composed of water. Therefore, an index of refraction for water (n = 1.333) was used to infer correct particle/droplet sizes from the WELAS raw data. According to Heim et al. (2008), the detection efficiency is ~1 for D (PSL) ≥1 µm, which translates to a water droplet diameter of D (water) ~ 1.4 µm. Thus, only WELAS data having a D (water) ≥ 1.4 µm will be considered in this study.

3 Methods

3.1 Classification of fog types

According to Tardif and Rasmussen (2007) developed fog is defined by a visibility lower than 1.6 km (1 land mile; however, in Europe it is common to use a threshold of 1 km; Haeffelin et al., 2010) for at least 30 min during a 50 min period. An automatic classification of fog events according to the scheme of Tardif and Rasmussen (2007) was carried out for the whole measurement period (2 October 2012 to 7 January 2013). The classification uses visibility, temperature, wind speed, precipitation, cloud cover and ceiling height as parameters to assign a type of fog to each event. The fog events were assigned to three different categories: (1) radi-
3.2 κ-Köhler theory

The equilibrium saturation vapour pressure (RH<sub>eq</sub>) over a solution droplet is described by the Köhler theory (Köhler 1936) considering the Raoult (solute) and Kelvin effects. Petters and Kreidenweis (2007) introduced a simple parametrization for the solute (Raoult) term in the Köhler equation. With this, the semi-empirical “κ-Köhler equation” is obtained (here expressed for the equilibrium supersaturation S<sub>eq</sub> as a function of the diameter of the solution droplet D):  
\[
S_{eq}(D) := RH_{eq}(D) - 1 = \frac{D^3 - (D^{dry})^3}{D^3 - (D^{dry})^3(1 - \kappa)} \exp \left( \frac{4\sigma_{s/a}}{RT} \rho_{w} \kappa \right)
\]  
where D<sup>dry</sup> is the dry particle diameter, σ<sub>s/a</sub> is the surface tension of solution/air interface (in our calculations the surface tension of pure water was taken), R is the universal gas constant, M<sub>w</sub> is the molar mass of water, T is the absolute temperature, ρ<sub>w</sub> is the density of water and κ is the hygroscopicity parameter, which depends on the particle chemical composition. Equation \([1]\) provides the relationship between S<sub>eq</sub> (RH<sub>eq</sub>, D<sup>dry</sup>, D<sup>0</sup>, and κ under equilibrium conditions, and forms the basis for various theoretical calculations done in the data analysis. For example, the critical supersaturation (S<sub>crit</sub>) of a particle with a certain dry size (D<sup>dry</sup>) and composition/hygroscopicity (κ) is obtained by numerically searching for the maximum of Eq. \([1]\) as a function of the droplet diameter (D).

The hygroscopicity parameter κ, corresponding to a pair of D<sup>dry</sup> and S<sub>crit</sub> is obtained by numerically solving the S<sub>crit</sub> = D<sup>dry</sup>−κ relationship for κ. This is used to infer the κ value from the CCNC and SMPS measurements, following the approach by Jurányi et al. (2011).

### 3.3 Reproducing the ambient total size distribution by combining dry SMPS with WELAS measurements

Figure [1] shows, as an example, the median total dry number size distribution (in brown) for a stratus lowering fog event on 12 November 2012. Since the total inlet samples the interstitial as well as the activated particles and dries them, all particles including droplet residuals are measured with the SMPS. With the assumption that the ambient relative humidity (RH) in the fog is approximately 100 %, the total dry size distribution measured by the SMPS (brown line in Fig. [1]) was recalculated to the corresponding ambient wet size distribution assuming hydrated (non-activated) particles (blue line in Fig. [1]) using κ-Köhler theory (Petters and Kreidenweis 2007) see also Sect. 3.2 and a fixed κ of 0.14 (overall median κ value discussed in Sect. 4.1).

The recalculated SMPS size distribution is comparable to the WELAS measurement of the size distribution at ambient RH (see green line in Fig. [1] in the common size range of 1.4 to 2.6 μm, which is a strong indication that the majority of these particles are not activated but hydrated particles in stable equilibrium. The total ambient size distribution for the complete diameter range 17 nm to ~10 μm was obtained by merging the recalculated SMPS measurement with

<table>
<thead>
<tr>
<th>Measured parameter(s)</th>
<th>Instrument</th>
<th>Accuracy</th>
<th>Measurement range</th>
<th>Time resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry aerosol number size distribution</td>
<td>Scanning Mobility Particle Sizer (SMPS)</td>
<td>Number conc.: ±20 % (20 &lt; D &lt; 50 nm)</td>
<td>D = 1–150 nm</td>
<td>6 min</td>
</tr>
<tr>
<td>Ambient aerosol and droplet number size distribution</td>
<td>Palas Wels-2000 Particle Counter</td>
<td>Number conc.: ±20 %</td>
<td>D = 1.4–10 µm (for water spheres)</td>
<td>5 min</td>
</tr>
<tr>
<td>Cloud condensation nuclei (CCN) number concentration</td>
<td>Continuous flow streamwise thermal gradient CCN chamber</td>
<td>Number conc.: ±10 %</td>
<td>SS = 0.05–0.6 % (20 min/ spectra)</td>
<td>1 s</td>
</tr>
<tr>
<td>Visibility</td>
<td>Degreanne DF20+ forward scatter sensor</td>
<td>&lt; 5 km: ±10 %</td>
<td>5–20 km: ±15 %</td>
<td>5 m–70 km</td>
</tr>
<tr>
<td>Liquid water content (LWC&lt;sub&gt;PVM&lt;/sub&gt;)</td>
<td>Particle Volume Monitor (PVM-100) PT-100 ATDM – MH13</td>
<td>&lt; 15 %</td>
<td>D = 3–50 µm</td>
<td>1 min</td>
</tr>
<tr>
<td>Temperature</td>
<td>Ambient aerosol and droplet Palas Welas-2000 Number conc.:</td>
<td></td>
<td>SS = 10–100 %</td>
<td>1 min</td>
</tr>
<tr>
<td></td>
<td>Particle Sizer (SMPS)</td>
<td></td>
<td>Number conc.: ±10 %</td>
<td></td>
</tr>
</tbody>
</table>

*measured by merging the recalculated SMPS measurement with the WELAS measurement of the size distribution at ambient RH (see green line in Fig. [1] in the common size range of 1.4 to 2.6 μm, which is a strong indication that the majority of these particles are not activated but hydrated particles in stable equilibrium.
the WELAS measurement, whereby the recalculated SMPS measurements were taken up to a diameter of 1.4 µm and the WELAS measurement covered the size range from 1.4 µm to 10 µm.

### 3.4 Retrieving the light scattering coefficients

To investigate the influence of hydrated particles and fog droplets on the light scattering during the fog events, the light scattering coefficient size distribution \( \frac{\partial b_s}{\partial \log D_w} \) was calculated from the ambient wet number size distribution \( \frac{\partial N_w}{\partial \log D_w} \).

\[
\frac{\partial b_s(D_w)}{\partial \log D_w} = \sigma(D_w) \cdot \frac{\partial N_w(D_w)}{\partial \log D_w} \tag{2}
\]

where \( \sigma(D_w) \) is the scattering cross section for the solar spectrum (American Society for Testing and Materials [ASTM]; [www.astm.org/]) of a spherical water droplet with diameter \( D_w \) and a refractive index of \( m = 1.333 - 0i \). The total light scattering coefficient, \( b_s \), is then obtained by integrating \( \frac{\partial b_s}{\partial \log D_w} \) over the whole diameter range.

### 3.5 Retrieving the threshold wet diameter that separates activated droplets from non-activated hydrated particles

Particles with a critical supersaturation above the effective peak supersaturation in the fog will remain in stable equilibrium and their size remains restricted to their stable equilibrium diameter at the ambient RH (~100%). Particles with a critical supersaturation below the effective peak supersaturation will be activated to droplets and keep growing until their water uptake pulls the ambient RH down to 100%. This will lead to a size separation between the non-activated but hydrated particles and the activated fog droplets, given a sufficient amount of excess water vapour to substantially grow the fog droplets. The resulting minimum in the ambient number size distribution between the modes of the non-activated but hydrated particles and the activated fog droplets approximately represents the size of the particles at the activation threshold, hereafter referred to as \( D_{\text{thres}} \). For most fog events no distinct minimum was detected in the number size distribution most probably due to limited growth of the few activated fog droplets. Therefore the surface size distribution of the aerosol was instead used to determine \( D_{\text{thres}} \) (see Fig. 2). In practice this was achieved by fitting a bimodal log-normal distribution to the wet surface size distribution obtained by merging the SMPS and WELAS measurements (see Sect. 3.3). This approach of determining \( D_{\text{thres}} \) is essentially equivalent to the method by Elias et al. (2014), except that they used the volume size distribution, which results in slightly larger threshold diameters as will be shown below.

The threshold diameter \( D_{\text{thres}} \), which represents the equilibrium diameter at RH = 100%, was then recalculated to the corresponding dry particle diameter using \( \kappa \)-Köhler theory (Peters and Kreidenweis 2007; see also Sect. 3.2) and a \( \kappa \) value of 0.14 (this is the reverse calculation of what is described in Sect. 3.3). The threshold diameter \( D_{\text{thres}} \) is considered to be slightly biased high, due to the \( D^2 \) weighting of the surface size distribution, and thus the corresponding dry size is considered to represent an upper estimate for the dry activation threshold diameter \( D_{\text{act}} \).

### 3.6 Retrieving the dry activation diameter from the interstitial and total particle size distributions

In the presence of a cloud, the dry activation threshold diameter \( D_{\text{act}} \) can be experimentally determined from the measured dry interstitial and total number size distributions via
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3.7 Retrieval of the effective peak supersaturation and associated uncertainties

Combining \( D_{\text{act}} \) with the particle hygroscopicity, obtained from the simultaneous CCNC measurements, makes it possible to infer the effective peak supersaturation of the cloud \( (\text{SS}_{\text{peak}}) \) using the \( \kappa \)-Köhler theory \citep{Peters2007}. A detailed description of this procedure can be found in Hammer et al. \citeyear{Hammer2014}.

The measured \( D_{\text{act}} \) and \( \kappa \) are used as input for Eq. \ref{eq:3} to infer the effective peak supersaturation. Thereby it is assumed that the activation occurred at the same temperature as measured 2 m above ground. The theoretical critical supersaturation corresponding to these values, which we define as \( \text{SS}_{\text{peak}} \) of the cloud, is then obtained with the \( \kappa \)-Köhler theory (Sect. 3.2).

Since two different methods for retrieving \( D_{\text{act}} \) were addressed in Sects. 3.5 and 3.6, two different \( \text{SS}_{\text{peak}} \) were retrieved: using \( D_{\text{act}}^{\text{upper}} \) and \( D_{\text{act}}^{\text{lower}} \) provides a lower and upper estimate for \( \text{SS}_{\text{peak}} \), respectively (subsequently referred to as \( \text{SS}_{\text{peak}}^{\text{upper}} \) and \( \text{SS}_{\text{peak}}^{\text{lower}} \)).

The experimental uncertainty for \( \text{SS}_{\text{peak}}^{\text{upper}} \) was estimated using the uncertainties described in Table \ref{table1}. The variability (25th/75th percentiles) of the \( \kappa-D_{\text{act}} \)–relationship from the time-resolved CCN measurements and the uncertainty from the temperature sensor was used as an estimate for the uncertainty of \( \kappa(D_{\text{act}}) \) (see Sect. 4.1 for further discussion). Applying these uncertainties for the retrieval of \( \text{SS}_{\text{peak}} \), a relative uncertainty of about 48\% (i.e., ca. one standard deviation) was estimated for \( \text{SS}_{\text{peak}}^{\text{upper}} \).

The uncertainty of \( \text{SS}_{\text{peak}}^{\text{lower}} \) is dominated by the uncertainty of \( D_{\text{act}}^{\text{wet}} \) inferred from the WELAS measurement. The uncertainty of \( D_{\text{act}}^{\text{wet}} \) is estimated to be \( \sim \pm 20\% \) associate with finding the minimum in the size distribution (the sizing uncertainty of the WELAS is only \( \sim \pm 9\% \) according to \cite{Kosati2014}). A relative uncertainty of \( \pm 3\% \) in \( \text{SS}_{\text{peak}} \) arises from a temperature uncertainty of \( \pm 10\% \). \( \text{SS}_{\text{lower}} \) is virtually independent of the \( \kappa \) value used to infer it from \( D_{\text{act}}^{\text{wet}} \) because in this approach the \( \kappa \)-Köhler theory is just used to extrapolate the Köhler curve over a very small change in RH and droplet diameter. On the other hand, the inferred \( D_{\text{act}}^{\text{upper}} \) would decrease by \( \sim 20\% \) if a \( \kappa \) value of 0.3 was assumed instead of 0.14.

The RH in the developed fog will stabilize slightly above 100\% RH, depending on the fog droplet sizes that are reached while buffering the excess water. The fact that the RH in the developed fog is not exactly known adds some uncertainty to the inferred \( \text{SS}_{\text{lower}} \) values. If the RH in the developed fog was assumed to be as high as 100.03\% (i.e. 0.03\% SS) instead of exactly 100.00\%, then the \( \text{SS}_{\text{lower}} \) would increase by 17\% (relatively). In the interest of providing a conservative estimate for \( \text{SS}_{\text{lower}} \), we assume an RH of exactly 100\% for this approach.

4 Results and discussion

During the ParisFog 2012/13 campaign 17 developed fog events were detected at the SIRTA site. Table \ref{table2} lists all fog events with the corresponding fog type, cut-off diameter at the interstitial inlet and median liquid water content (LWC) measured by the PVM (LWC\textsubscript{PVM}).

The next nine columns show the median effective peak supersaturations (\( \text{SS}_{\text{peak}}^{\text{lower}} \) and upper estimate), median dry activation diameter (\( D_{\text{act}}^{\text{lower}} \) and lower and upper estimate), median threshold diameter (\( D_{\text{act}}^{\text{wet}} \)), the scattering coefficients for the modes of hydrated particles (\( b_{\text{hydr}} \)) and the activated droplets up to a diameter of 10µm (\( b_{\text{drop}} \)).
tional contribution of the non-activated but hydrated particles to light scattering of \(b_{s,\text{hyd}}\) to \(b_{s,\text{dry}}\), and particle extinction coefficient (pec) that are discussed in Sect. 4.2 and [3,3]. Seven fog events of the type STL and seven fog events of the type RAD were detected. One fog event of the type PREC was detected, however, neither the SMPS nor the WELAS measured the latter fog type, therefore no results about this event are presented.

Figure 4 gives an overview of the most important meteorological parameters, the fog presence and type (in different color bars), and the total particle number concentration during the campaign. The temperature slightly decreases from the beginning of the campaign towards the end with a minimum value of \(-6^\circ\text{C}\) and a maximum value of \(23^\circ\text{C}\) (Fig. 4a). The wind speed at the site was rather moderate during the whole campaign ranging from 0 to 11.3 m s\(^{-1}\) (Fig. 4b). There is a high frequency of wind coming from the northeast and thus polluted air from the Paris metropolitan area is transported to the site (Haefelin et al., 2005). In Fig. 4c, the total particle number concentration is depicted and reveals rather high pollution transported from Paris with northeastern wind direction. Maximum values of 12 800 cm\(^{-3}\) and a median value of 2800 cm\(^{-3}\) in the total particle number concentration were encountered. However, the studies of Crippa et al. (2013a) found at the same site that a major part of the fine particulate matter in Paris is contributed by the regional background rather than by local pollution. Thus, the higher pollution with northeastern wind directions measured at the SIRTA site may be attributed to more continental influence compared to the cleaner western sector, but also to the local influence of road traffic and wood burning emissions (Crippa et al., 2013b) as will be further discussed in Sect. 4.1.

Figure 3 presents the visibility measured by the Degreanne forward scatter sensor DF20+ instrument on a log-scale with the threshold at 1 km (dotted line) defining developed fog. Events when the visibility decreased to values between 1 and 5 km are defined as mist or quasi-fog. Such events were investigated at the SIRTA in detail (Elias et al., 2009; Haefelin et al., 2013). Median visibility ranges of 244 m and 211 m were observed for developed RAD and STL fogs during ParisFog 2012/13, respectively, reaching down to a minimum of 107 m (1 h average). In earlier campaigns minimum values down to \(~50\) m were observed at the SIRTA site (Haefelin et al., 2010).

### 4.1 Particle hygroscopic properties during ParisFog 2012/13

The hygroscopicity of aerosol particles is relevant for many atmospheric processes; it can be described with the hygroscopicity parameter \(\kappa\) (Sect. 3.2), which is required in this study to infer the \(\text{SS}_{\text{peak}}\) from the observed activation diameters. The hygroscopicity parameter as a function of particle dry size, \(\kappa(D_{\text{dry}})\), was determined from simultaneous total polydisperse CCN number concentration and aerosol size distribution measurements, following the approach described in Jurányi et al. (2011) and Hammer et al. (2014). While total aerosol size distributions are available for the whole period, there are some gaps of the measurement period for the CCN measurements. Therefore, median data of \(\kappa(D_{\text{act,CCNC}})\) were used to infer \(\text{SS}_{\text{peak}}\) for all the fog events of ParisFog 2012/13.

Figure 5 shows the median \(\kappa\) values observed during ParisFog 2012/13. The median \(\kappa\) value decreased from 0.17 at \(D_{\text{dry}} = 69\) nm to 0.09 at \(D_{\text{dry}} = 295\) nm and then increased to 0.17 at 310 nm. The abrupt change in \(\kappa\) between 295 and 310 nm dry diameter is unreasonable and may be attributed to an increased experimental uncertainty of CCN measurements at very low SS. In this study we have chosen a fixed \(\kappa\) value of 0.14, which represents a mean value across the size range from 205 to 330 nm, for inferring \(\text{SS}_{\text{peak}}\). The \(\kappa\) values observed in this study are very close to the previously reported winter-time values for the same site (Jurányi et al., 2013) \(\kappa = 0.08-0.24\) for \(D_{\text{dry}} = 50-177\) nm as well as Paris city centre (Kamilli et al., 2014), \(\kappa = 0.17\) for \(D_{\text{dry}} = 285\) nm). The \(\kappa\) values reported for Paris are substantially lower than the observed and modelled average value of \(\kappa \approx 0.3\) for continental sites (Andreae and Rosenfeld, 2008; Pringle et al., 2010). This low \(\kappa\) value is most likely due to the influence of non- or less-hygroscopic road traffic and residential woodland burning emissions (Crippa et al., 2013b) which lowers the mean hygroscopicity of the aerosol substantially (Baltensperger et al., 2002; Labbé et al., 2013).

The variability in the \(\kappa\) value over the whole period of ParisFog 2012/13 is indicated by the shaded area between the 25th and 75th percentiles of all data during the three months in Fig. 5. The variability in time in the values is fairly small, particularly between diameters of about 100 nm and 250 nm. At larger particle diameters (250 nm to 350 nm the range between the 25th and 75th percentile increases somewhat). This low variability and the fact that \(\text{SS}_{\text{peak}}\) is insignificantly sensitive to \(\kappa\), permit the use of averaged \(\kappa\) values instead of time-resolved \(\kappa\) values derived from simultaneous CCN measurements.

#### 4.2 Observed fog activation properties

The droplet diameters observed during the events are in the range where very large and hygroscopic particles can exist in stable equilibrium. This brings up the question whether supersaturation and true droplet activation occurred at all during fog formation. We are confident that this was the case as particles on the stable side of the Köhler curve, which have a clearly defined equilibrium diameter, cannot buffer the RH at 100 % by uptake or release of water vapor, if the ambient temperature varies. Thus, if the air cools below the temperature that corresponds to 100 % RH, then the RH will exceed 100 % and the peak supersaturation will only be reached...
larger water fluxes resulting in larger growth rates such that the case of fog. Therefore the activated droplets experience experienced by the air parcel are generally larger than in drated, particles. In non-fog cloud types, the cooling rates the activated fog droplets from the non-activated, but hy-
portant to know which ambient threshold diameter separates the activated particles (Noone et al., 1992a). Thus, it is im-
cut-off of 5 µ
reduce the RH back to 100 % RH.
when the activated droplets have taken up enough water to RH back to 100 % RH.

For measuring the interstitial aerosol a size cut-off of 1 or 2 µ
was used during the campaign (see Sect. 2.2). In an-
other fog-campaign performed in the Po Valley, Italy, a size cut-off of 5 µ
was used to distinguish the interstitial from the activated particles (Noone et al., 1992a). Thus, it is im-
portant to know which ambient threshold diameter separates the activated fog droplets from the non-activated, but hy-
drated, particles. In non-fog cloud types, the cooling rates experienced by the air parcel are generally larger than in the case of fog. Therefore the activated droplets experience larger water fluxes resulting in larger growth rates such that the two modes of hydrated aerosols and activated droplets are much more distinct in diameter for clouds (e.g. at the Jungfraujoch, Switzerland, Henning et al., 2002, or for marine stratus clouds, Baltic Sea, Ditas et al., 2012) than observed in fog, as we will see in the following.

Figure 4 shows the ambient aerosol number size distribution and Fig. 5 the corresponding normalized surface size distribution for the fog event F7 detected on 4 November 2012. The aerosol size distribution at ambient RH was obtained by complementing the direct WELAS measurement (for diameters larger than 1.4 µ
with the SMPS measurement of the total aerosol dry size distribution recalculated to RH = 100 % (for the diameter range smaller than 1.4 µ
,
of the threshold diameter, $D_{\text{threshold}}$, of the orange markers in Fig. 6b, is considered to be an estimate size distribution below the fog droplet mode, shown with face size distribution (Fig. 6a). The minimum in the surface droplets appear as a distinct mode in the normalized surface distribution (Fig. 6a). The activated but hydrated aerosol particles. The activated fog SMPS measurement recalculated to RH=100 % (for $D_{\text{wet}}$) and/or less hygroscopic CCN that got truly activated (e.g. as detailed in Sect. 3.5). Droplets with diameters larger than $2 \mu m$ are only observed at times with developed fog, i.e. when the visibility is below the threshold value of $\sim 1 \text{km}$. This suggests that these large droplets represent activated fog droplets, while droplets with diameters $<2 \mu m$ are non-activated but hydrated aerosol particles. The activated fog droplets appear as a distinct mode in the normalized surface size distribution (Fig. 6a). The minimum in the surface size distribution below the fog droplet mode, shown with orange markers in Fig. 6a, is considered to be an estimate of the threshold diameter, $D_{\text{wet,threshold}}$, for fog droplet activation, as detailed in Sect. 3.5. It is important to note that, large and very hygroscopic CCN with critical droplet diameters above $5 \mu m$ may potentially remain in stable equilibrium even under developed fog conditions, coexisting with smaller and/or less hygroscopic CCN that got truly activated (e.g. Phinney et al., 2003). The reason for this phenomenon are kinetic limitations (Nenes et al., 2001): depending on the conditions, the CCN with smaller critical wet diameter require less time to grow across their critical size compared to the CCN with much larger critical diameter. However, this phenomenon does not invalidate data analysis approach for retrieving the $D_{\text{wet,threshold}}^\text{act}$ which uses the minimum in the droplet size distribution between the modes from unactivated droplets in stable equilibrium and truly activated droplets, because the large CCNs would show up in the uppermost tail of the droplet size distribution.

The cut-off diameter of $1 \mu m$ applied at the interstitial inlet for the example in Fig. 4 is always clearly below the wet activation threshold diameter. Thus, a significant fraction of the non-activated but hydrated particles are removed from the interstitial inlet, in addition to the fog droplets which are supposed to be removed. In those cases the dry activation diameter ($D_{\text{act}}$, as explained in Sect. 3.6) reflects the dry size corresponding to the hydrated particles with an equilibrium size at ambient RH that is equal to the cut-off of the interstitial inlet. Thus, the inferred $D_{\text{act}}$ is a lower estimate for the dry activation threshold diameter and is called $D_{\text{act,lower}}$. The bias introduced by this artifact is more significant the lower the cut-off of the interstitial inlet is. Thus, the results obtained from measurements with the $2 \mu m$-cut-off are expected to be closer to the true value than those obtained with the $1 \mu m$-cut-off. This is illustrated with the ambient aerosol number and surface size distributions observed during fog event F11 (Fig. 7a and b), when a $2 \mu m$-cut-off was applied at the interstitial inlet. In this case, the wet activation threshold diameter is closer to the inlet cut-off and thus the bias in the retrieved $D_{\text{act,lower}}$ is expected to be small.

Figure 7c shows the dry activation diameters $D_{\text{act,upper}}$ and $D_{\text{act,lower}}$, inferred from the wet activation threshold diameter and the interstitial/total dry size distribution measurements for fog event F11, respectively (see Sects. 3.5 and 3.6 for the methodology). The difference between $D_{\text{act,upper}}$ and $D_{\text{act,lower}}$ is small when the wet activation threshold diameter is around the cut-off of the interstitial inlet and larger at other times.

The estimate of $D_{\text{act}}$ combined with the particle hygroscopicity from CCN measurements are the basis to infer the effective peak supersaturation ($SS_{\text{peak}}^\text{act}$) of fog according to the methodology addressed in Sect. 3.2. $\kappa$ value of 0.14, representing the averaged CCN measurement near activation diameters (see Sect. 3.2 and Fig. 5), was used to infer $SS_{\text{peak}}$ with Köhler theory. Figure 7d shows the lower and upper limit estimates of the effective peak supersaturation, $SS_{\text{lower}}^\text{act}$ and $SS_{\text{upper}}^\text{act}$, corresponding to the upper and lower limit estimates of the dry activation diameter, $D_{\text{act,upper}}$ and $D_{\text{act,lower}}$, respectively. The results for the fog event F11 indicate a very low supersaturation in the range between $\sim 0.016$ to 0.113 %.

As mentioned above, a rather low $\kappa$ value of 0.14 as measured at dry diameters $<300 \mu m$ is used to infer $SS_{\text{peak}}^\text{act}$.
The variability of the effective peak supersaturation values is events are provided in Table 2. The lower estimates for the dry activation diameter, $D_{\text{act}}^{\text{lower}}$, are systematically smaller for the fog events F4 to F9, when the 1 µm-cut-off was applied at the interstitial inlet, compared to the results for fog events F1 to F3 and F11 to F15, obtained with the 2 µm-cut-off. This difference in $D_{\text{act}}^{\text{lower}}$ between the two subsets is artificial and can be attributed to the larger low bias introduced by the 1 µm-cut-off. The fact that the upper limit estimates of the dry activation diameter, $D_{\text{act}}^{\text{upper}}$, do not exhibit a systematic difference between the two subsets, excludes a difference in the fog properties as a cause. The true activation diameter is likely between $D_{\text{act}}^{\text{upper}}$ and $D_{\text{act}}^{\text{lower}}$ from the measurements with the 2 µm-cut-off.

All fog events feature rather high median $D_{\text{act}}^{\text{lower}}$ and $D_{\text{act}}^{\text{upper}}$ indicating that only a small fraction at the upper end of the particle size distribution is able to activate to fog droplets. The range of dry activation diameters observed in this study overlaps with the range of typical $D_{\text{act}}$ values reported in other fog studies ($\sim 300 \text{ to } 500 \text{ nm}$; e.g. Noone et al. [1992a], Ming and Russell [2004]). However, the dry activation diameters observed in the fog are considerably larger than those observed and/or inferred within stratus or cumulus clouds (e.g. Ditas et al. [2012], Hammer et al. [2014], Hudson and Rogers [1986], Krueger et al. [2013], McFiggans et al. [2006]) due to the lower SS$_{\text{peak}}$ encountered in fog.

The effective peak supersaturations determined for all fog events during ParisFog 2012/13 are shown in Fig. 8. For the upper estimate, the results from events F1–F15 (2 µm-cut-off) are expected to be closer to the true value for the reasons explained above. The effective peak supersaturation is always very low with limiting values between 0.016% and 0.113%. Differences in the observed SS$_{\text{peak}}$ values between different fog events are of similar magnitude as the accuracy. Nevertheless, these differences reflect true differences of the fog properties, as the small point-to-point variability of adjacent data points indicates a relatively high precision. The median effective peak supersaturation falls between SS$_{\text{peak}}^{\text{lower}} \approx 0.03\%$ and SS$_{\text{peak}}^{\text{upper}} \approx 0.05\%$ (see Table 2).
Figure 9. 10th, 25th, 50th (median), 75th and 90th percentiles (box-plot) and mean value (cross) of the effective peak supersaturation (SS\textsubscript{peak}) for the upper and lower estimate for ParisFog 2012/13. For the upper estimate the data was split according to the cut-off diameter at the interstitial inlet, 1 µm (PM\textsubscript{1}) and 2 µm (PM\textsubscript{2}).

The results shown in Fig. 4 show that a higher particle number concentration while wind directions from the Paris city center were measured (sector between $\sim 0^\circ$ and $\sim 90^\circ$). However, neither the obtained SS\textsubscript{peak} nor the $\kappa$ values show any pattern with the wind direction. Laborde et al. (2013) showed, through the combined analysis of aerosol composition and hygroscopicity distribution data measured at the SIRTA site in Winter 2010, that a dominant number fraction of the particles with a diameter of 110 nm often originates from local emissions from within Paris, while the dominant fraction of the particles with a diameter of 265 nm can be attributed to the background aerosol. This size dependence of local influence can be explained by the fact that the size distribution of primary particle emissions from combustion sources peaks at rather small sizes clearly below the maximum of the background aerosol size distribution. The observations of this study showed that only particles with dry diameters larger than $\sim 300$ – $500$ nm are able to act as condensation nuclei for fog droplets due to the low peak supersaturation. This finding is consistent with the small number concentration of fog droplets usually measured at the SIRTA site (Elias et al., 2014). Therefore, the local emissions comprised of small particles, don’t have a substantial effect on the resulting fog droplet number concentration. The fact that the freshly emitted particles are less hygroscopic than the background aerosol (Laborde et al., 2013), which shifts the activation threshold diameter for local emissions even higher up, further amplifies the dominant influence of background aerosol particles. Crippa et al. (2013a) showed, by parallel measurements of fine particulate matter (PM1) at three measurement sites across Paris in winter 2010, that variations of aerosol mass concentration and composition are dominated by regional scale influence, while local emissions only give a minor contribution. This is consistent with the above-mentioned findings from Laborde et al. (2013), given the fact that the dominant contribution to particle mass and bulk composition comes from larger particles, which are mainly from the background aerosol. The regional scale emission may potentially have some influence on fog properties, for example by growing background aerosol mode particles across the activation threshold dry diameter through condensation of secondary aerosol matter. However, this potential effect cannot be quantified from the data set available here.

4.2.2 Possible influences of in-fog processes on measured $D_{\text{act}}$ and inferred SS\textsubscript{peak}

The size distributions of the total, interstitial and droplet residual particles may be altered by in-fog processes such as fog droplet sedimentation, entrainment of subsaturated air, in-cloud scavenging of interstitial particles, coalescence of fog droplets, and droplet processing, which includes condensation of semi-volatile aerosol components or aqueous phase heterogeneous formation of secondary aerosol within the droplet (e.g. Noone et al. [1992a] [Henning et al. 2014]). These processes can potentially lead to a bias in the measured $D_{\text{act}}$ compared with the true dry activation diameter at the time of fog formation. A detailed sensitivity analysis, provided in the supplementary information, revealed that the measured $D_{\text{act}}$ may be larger (more likely) or smaller (less likely) compared to the true $D_{\text{act}}$ due to the effects of in-fog processes. These artefacts are most likely smaller than $\sim 15\%$, which is within the specified uncertainty of the measured $D_{\text{act}}$. 
Visibility is dramatically reduced during the presence of fog. It can decrease from a few kilometers to a few meters within minutes (as occurred for example on 30 November 2012, F15). However, it was observed that only a few of the larger particles usually are able to activate to fog droplets (10 to 15 cm). Visibilities are the smallest and largest particle diameters) were found between 0.06 and 0.27, and centered at 0.14. These values are in the same range as observed during the ParisFog 2012/13 field campaign, performed at the semi-urban site SIRTA in Palaiseau, close to Paris, 17 developed fog events were observed and examined regarding their aerosol-to-fog droplet activation properties. Aerosol and droplet size distributions were obtained at ambient relative humidity. The activated fraction of the particles was acquired using total and interstitial particle dry size distribution measurements. CCN number concentrations were measured in order to obtain an estimate of the total light scattering of all particles and droplets, the WELAS data would need to be complemented with a fog droplet probe. Another method is to calculate the particle extinction coefficient (pec) from the visibilimeter data using the Koschmieder equation (Koschmieder 1925; Harrison 2012) as has been done in Elias et al. (2009): pec = −ln(Cv) visibility

Cv is the visual contrast, which is defined at 5% for the visibilimeter. The pec is retrieved for a halogen lamp spectrum (in the wavelength range 350–900 nm peaking at 550 nm; spectrum used from www.uvguide.co.uk, which is similar to the visible part of the solar spectrum) and is listed in Table 2. For comparison, Fig. 10 shows the median b_s, as described in Sect. 4.3. For comparison, Fig. 10 shows the median b_s, when large droplets are present. Nevertheless, the conclusion that the hydrated but non-activated particles give a significant contribution to the visibility reduction remains valid also when considering the ratio $b_{s,hyd}/b_{s,drop}$.
in earlier studies at SIRTA and Paris city centre. These rather low values likely indicate substantial influence of road traffic and wood burning emissions.

Two alternative approaches were applied to investigate the fog droplet activation process. The wet activation threshold diameter, separating the activated fog droplets from the non-activated but hydrated particles, was found to be around 2.6 \( \mu m \). The median dry activation diameter was estimated to lie between 364 and 450 nm. This implies a median peak supersaturation between 0.03 % and 0.05 % for ParisFog 2012/2013, which is in good agreement with literature values.

The hydrated particles were estimated to contribute on average \( \sim 41 - 68 \% \) to total light-scattering during the developed fog periods.

This study revealed a very weak separation between the activated fog droplets and the non-activated but hydrated particles. This makes it difficult to use an interstitial inlet for separating the non-activated particles from the activated fog droplets. Thus, great care has to be taken to choose the ideal inlet cut-off, possibly variable in time, in order to avoid or minimize biases that can be introduced by removing too many small or too few large particles in the inlet, if the cut-off falls into one of the two modes rather than in between them.

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