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Atmospheric Chemistry and Physics

Seasonal variation of aerosol size distributions in the free troposphere and residual layer at the puy de Dôme station, France

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Abstract. Particle number concentration and size distribution are important variables needed to constrain the role of atmospheric particles in the Earth radiation budget, both directly and indirectly through CCN activation. They are also linked to regulated variables such as particle mass (PM) and therefore of interest to air quality studies. However, data on their long-term variability are scarce, in particular at high altitudes. In this paper, we investigate the diurnal and seasonal variability of the aerosol total number concentration and size distribution at the puy de Dôme research station (France, 1465 m a.s.l.). We report a variability of aerosol particle total number concentration measured over a five-year (2003–2007) period for particles larger than 10 nm and aerosol size distributions between 10 and 500 nm over a two-year period (January 2006 to December 2007). Concentrations show a strong seasonality with maxima during summer and minima during winter. A diurnal variation is also observed with maxima between 12:00 and 18:00 UTC. At night (00:00–06:00 UTC), the median hourly total concentration varies from 600 to 800 cm^{-3} during winter and from 1700 to 2200 cm^{-3} during summer. During the day (08:00–18:00 UTC), the concentration is in the range of 700 to 1400 cm^{-3} during winter and of 2500 to 3500 cm^{-3} during summer. An averaged size distribution of particles (10–500 nm) was calculated for each season. The total aerosol number concentrations are dominated by the Aitken mode integral concentrations, which drive most of the winter to summer total concentrations increase. The night to day increase in dominated by the nucleation mode integral number concentration. Because the site is located in the free troposphere only a fraction of the time, in particular at night and during the winter season, we have subsequently analyzed the variability for nighttime and free tropospheric (FT)/residual layer (RL) conditions only. We show that a seasonal variability is still observed for these FT/RL conditions. The FT/RL seasonal variation is due to both seasonal changes in the air mass origin from winter to summer and enhanced concentrations of particles in the residual layer/free troposphere in summer. The later observation can be explained by higher emissions intensity in the boundary layer, stronger exchanges between the boundary layer and the free troposphere as well as enhanced photochemical processes. Finally, aerosols mean size distributions are calculated for a given air mass type (marine/continental/regional) according to the season for the specific conditions of the residual layer/free troposphere. The seasonal variability in aerosol sources seems to be predominant over the continent compared to the seasonal variation of marine aerosol sources. These results are of regional relevance and can be used to constrain chemical-transport models over Western Europe.

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1 Introduction

The seasonal and diurnal variation of aerosol parameters such as $PM_{2.5}$ and PM_{10} mass concentrations have been extensively documented in various environments (Putaud et al., 2004; Russel et al., 2004; Karaca et al., 2005; Ho et al., 2006). However, less information is available for the number related parameters such as particle number concentrations and size distributions. This is a considerable limitation because these variables are amongst the most relevant to constrain (1) directly the light scattering and absorption properties of the aerosols and (2) the number of CCN which in turn

play an important role in the Earth radiation budget. Important parameters such as the scattering coefficient are strongly particle size dependent. Knowledge of these variables is also relevant to derive cloud condensation nuclei (CCN) concentration and, thus, the cloud droplet populations. Similarly, information on the spatial and temporal variability of number concentration and size is of great interest to constrain global and regional modeling and to investigate processes involved in particle formation and sinks.

Particle number concentrations and size distributions are also linked to the particle mass (Van Dingenen et al., 2005) and, for both climate and air quality studies, aerosol number concentration and size are often more pertinent parameters than the aerosol mass. In fact, the aerosol number concentration is dominated by its fine (particle diameter (D_p)$<1\,\mu$m) and specially ultrafine (D_p $<0.1\,\mu$m) fractions. Because of the two competing processes of homogeneous nucleation and growth of particles by condensation of gas-phase species onto pre-existing particles, the number concentration of particles smaller than 20 nm has been observed to be anti-correlated with the aerosol volume and mass (Rodriguez et al., 2005). Hence, a reduction in the aerosol volume would result in an increase of the aerosol number concentration of the ultrafine particles. A more accurate knowledge of particle number and size is therefore clearly needed.

Long-term monitoring of aerosol number concentration and size distribution has been performed at several measurement sites in particular in the boundary layer at urban locations (Wehner and Wiedensohler, 2003; Ganguli et al., 2006; lonati et al, 2006; Tuch et al., 2006), at rural and remote sites (Birmili et al., 2001; Mäkelä et al., 2000; Tunved et al., 2003; Rodriguez et al., 2005), in the artic atmosphere (Komppula et al., 2003), in marine environments (Satheesh et al., 2006; Yoon et al., 2006), and in the free troposphere (Nyeki et al., 1998; Weingartner et al., 1999; Osada et al., 2003).

Current knowledge of aerosol number size distributions has generally allowed to divide the number size distribution into a Nucleation mode (3–20 nm) representative of recent new particle formation, an Aitken mode (40–80 nm), and an accumulation mode (100–300 nm) representing more aged particles. The aerosol size distributions have been classically described as a function of the air mass type (marine, continental, mixed) (Birmili et al., 2001; O'Dowd et al., 2001; Tunved et al., 2005). However, even within the same air mass type, the aerosol is rapidly transformed through the influence from additional sources, or dilution, deposition and coagulation processes within 36 hours, leading to major aerosol size and concentration differences between locations separated by a few hundreds of kilometres (Tunved et al 2005). In addition to the clear air mass type dependency of aerosol properties for a given location, a pronounced seasonal variability has been observed in many environments. Marine aerosols in the boundary layer have shown a seasonal variation with a maximum number concentration during summer and a minimum during winter (Yoon et al., 2007). On the contrary, some continental aerosols show maximum concentrations during winter due to an accumulation of the particles within a low boundary layer height at night (Rodriguez et al., 2005), and other maximum concentrations during spring due to a maximal frequency of nucleation events (Komppula et al, 2000; Tunved et al., 2003). Hence, in order to use as realistic inputs as possible for climate modelling, it is necessary to deliver air mass based aerosol climatology for each season and representative of a specific area.

The observation of the seasonal and diurnal variation of atmospheric variables at remote high altitude sites brings additional valuable information on the horizontal and vertical extent of the anthropogenic influence on the larger regional and global atmospheric scales. Firstly because continuous measurements of fine aerosol size distributions and number concentrations from elevated sites are scarce in Europe (Nyeki et al., 1998; Weingartner et al., 1999), and secondly because mountain sites are often rather influenced by long-range transport than by local sources and, hence, provide information on the aerosol variability at the regional scale. In this paper, we report diurnal and seasonal variability of aerosol particles total number concentrations measured over a six-year period (2002–2007) and measurements of aerosol size distributions measured over a two-year period (January 2006 to December 2007) with special focus on the variability linked to long-range transport..

2 Sampling techniques and site

The puy de Dôme research station is located at 1 465 m above the sea level in central France (45°46′N, 2°57′E). The station is surrounded by a protected area where fields and forests are predominant. The city of Clermont-Ferrand (150 000 inhabitants) is located 16 km east of the station at 396 m a.s.l. Previous work at the station shows that the influence of the city on the puy de Dôme measurements is fairly limited, especially during nighttime. Meteorological parameters including wind speed and direction, temperature, pressure, relative humidity and radiation (global, UV and diffuse), atmospheric trace gases (O_3, NO_x, SO_2, CO_2), and particulate equivalent black carbon (eqBC) are continuously monitored throughout the year. Winter temperatures vary typically from -5 to +1 °C and summer temperatures from 10 to 20°C. Westerly winds are dominant. During the November–April period road access to the station is restricted while it is open to public transport for the rest of the year. Traffic generally stops 500 m away from the sampling station and does not influence sampled air composition. In fact, CO and NO_x concentrations are higher in the November-April period than in the May–September period, indicating that a local contamination is not observed.

Because the puy de Dôme station is more than 50% of the time in clouds, aerosol sampling is performed through a whole air inlet (WAI) which samples during cloudy

conditions both aerosols and cloud droplets which are subsequently evaporated to cloud residues. Based upon theoretical considerations, the WAI is capable of efficiently sampling droplets $<35\mu$m for wind-speeds $<10\,\mathrm{ms}^{-1}$, thus, representing the majority of the cloud droplets population in a typical cloud (Sellegri et al., 2003). The resulting aerosol size distribution is expected to be equivalent to that obtained after the natural dissipation of a cloud. Wind speed is decreased in the vicinity of the WAI by metallic fences ensuring efficient sampling even at elevated wind speeds. Total aerosol concentrations were measured from 2002 to 2005 using a TSI Inc. 3010 CPC for particles sizes larger than 10 nm. Discontinuities in the measurements were due to instrumental failures or use of the instrument for measurement campaigns elsewhere. This explains the lack of data during the first half of 2003 and 2005. The diffusion losses in the inlet are calculated to be less than 5% for particles larger than 15 nm. From January 2006 to December 2007 a SMPS (Scanning Mobility Particle Sizer) monitored the particle number size distribution (10–500 nm) through the WAI. The SMPS comprised a ^{63}Ni neutralizer, a custom-made Differential Mobility Analyzer (DMA) (Villani et al., 2007) selecting negatively charged particles, and a TSI Inc. 3010 Condensation Particle Counter (CPC). The SMPS is operated continuously with a two-minute time resolution. The SMPS inversion takes into account the CPC efficiency and the charge equilibrium state (Wiedensohler, 1988) using 108 channels over the 10–500 nm range on the up-ramp of the voltage scan. The process of nucleation itself can not be examined in the present study, but some information can be extracted on the occurrence of new ultrafine particles formed by secondary processes, as 10-nm particles are of primary origin only when sampled very close to their source. Data quality of the size-distribution was first checked by comparing the integrated SMPS number concentrations with total concentrations measured by an additional TSI Inc. 3010 CPC connected to the same sampling line over limited periods, and second during several inter-calibration procedures within the EUSAAR project (www.eusaar.net). During the 2008 intercomparison workshop, the number concentration particles measured with the SMPS was compared to a reference CPC counter and agreed within 20% for laboratory-generated ammonium sulfate particles, and 5% for ambient aerosols. Hence, we believe that the charging efficiency of the ^{63}Ni neutralizer is insufficient for heavily charged nebulized particles but adequate for ambient measurements. Losses in the DMA were reduced compared to a TSI-type 3081 column after the DMA inlet was modified (Villani et al., 2008). Actually, the SMPS showed one of the highest concentrations of ultrafine particles among the 11 SMPS present during the intercalibration, indicating that diffusion losses inside the instrument are limited. Size determination with latex 200 nm spheres agreed within 4% with a deviation underestimating the reference particle size.

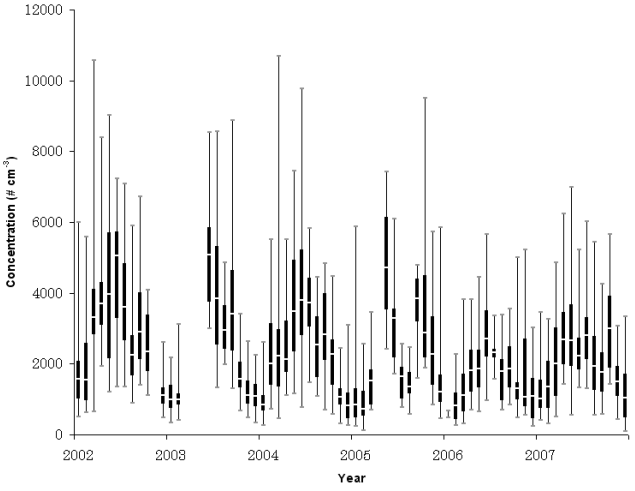

Fig. 1a. Monthly median total number particle concentrations (Dp>10 nm), 25–75th percentile and minimum-maximum ranges over the 2002-2007 period.

In the framework of the present paper, the total number concentration is derived from direct CPC 3010 measurements from 2002 to 2005 and for 2007, and from integrated SMPS measurements for the whole year 2006 (no CPC measurements were available during 2006). The size distribution analysis discussed in this paper has been performed in the January 2006 to December 2007 period. Aerosol particle concentrations and size distributions are given for ambient temperature and pressure. The average temperature at the puy de Dôme during winter, spring, summer and autumn are -1.7±1.8, 3.4±3.3, 12.2±2.9, 5.9±4.0 (°C), respectively, and the respective average pressures are 852.4±3.8, 851.3±3.6, 856.4±2.4, 854.4±3.2 (mbar), respectively.

Air mass three-day back trajectories were calculated using the HYSPLIT transport and dispersion model and/or READY website (http://www.arl.noaa.gov/ready.html) (Draxler and Rolph 2003, Rolph 2003) with a resolution of 6 hours. Because the turnover time of aerosol particles has been evaluated to be from 1.6–1.7 days for nuclei size ranges, to 2.4 days for 200 nm particles (Tunved et al., 2005), we arbitrarily limit the back trajectories calculations to 72 h.

3 Seasonal and diurnal variability

3.1 Particle number concentrations

Monthly median number particle concentrations were calculated from the TSI 3010 CPC five-minute number concentrations and integrated SMPS number concentrations in order to provide a clear picture of the concentrations long-term variability (Fig. 1a). We observe a clear seasonal variation over six years with maxima during summer and minima during winter. The average daily aerosol concentration is

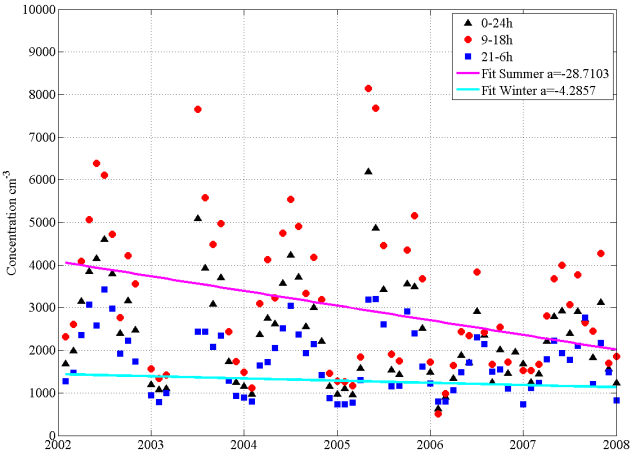

Figure 1b. Nightime and daytime monthly median total number particle concentrations (Dp>10 nm) over the 2002–2007 period

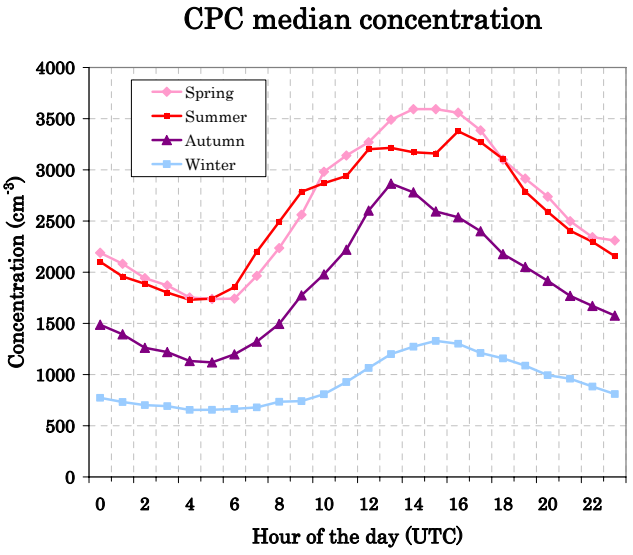

Fig. 2. Median diurnal variations (from 00:00 to 24:00 UTC) of total number concentrations obtained from CPC concentration calculated for each season over the 2002-2005 and 2007 period.

2500 cm^{-3} in summer and 900 cm^{-3} in winter, respectively. The total carbonaceous mass concentration was also found to be more than two times higher during summer compared to winter at the puy de Dôme (Pio et al., 2007). Seasonal variations of the total particle number concentration have been documented in several environments (Yoon et al., 2007; Rodriguez et al., 2005; Komppula et al., 2000, Nyeki et al., 1998; Weingartner et al., 1999; Osada et al., 2003; Van dingenen et al., 2005) with maxima differing according to the site. Compared to the extensive study of Van Dingenen et al. (2004) for European sites, the puy de Dôme concentrations fall between those measured at the high altitude site of Jungfraujoch, Switzerland, and those measured at the boundary layer site of Aspvreten in Sweden. A seasonal variation was not systematically observed by Van Dingenen et al. (2004) for all European sites, showing that the combination of source strength, dilution (due to the boundary layer height), and sink (by precipitation) produce very different features amongst European sites.

From the rather long data set presented in this work, we observe a trend in the aerosol number concentrations with a minimum in 2006. The trend originates from variations in the summer concentrations, while winter concentrations remained rather constant with time during this period. The summer concentrations decrease with a rate of 350 cm^{-3} $year^{-1}$ (9%). It is difficult at this stage to provide an explanation to this decreasing trend based on a limited number of years. There is a clear need to verify whether similar trends are observed at other high altitude stations in Europe. We can notice that trends in CN concentrations are paralleled with trends in summer temperatures (-0.9°C $year^{-1}$ with respect to -0.36°C $year^{-1}$ during winter). The link between a decrease in temperature and a decrease in aerosol number concentrations could be attributed to several reasons such as temperature-related changes in biogenic emissions, enhanced photochemical processes associated with sunny summers, or stronger vertical transport to the puy de Dôme height associated with higher temperatures. However, the potential link between temperature and CN concentrations is clearly indirect and beyond the scope of the present study.

All of the processes mentioned above should lead to higher concentrations during the day compared to during the night. Figure 1b shows that the trend in decreasing aerosol concentrations over the years is indeed more detectable in the daytime concentrations than in the nighttime concentrations. The diurnal variability of the median concentration has been calculated for four different seasons corresponding to the maximum concentrations (June-July-August: summer), the minimum concentrations (December-January-February: winter) and intermediate concentrations (March-April-May: spring and September-October-November: autumn) (Fig. 2). The diurnal variation of the median number concentration shows high values between 12:00 and 18:00 UTC for all seasons. At night (00:00-06:00), the median hourly total concentration varies from 500 to 750 cm^{-3} during winter and from 2000 to 2750 cm^{-3} during summer. During the day (08:00–18:00), the concentration ranges from 700 to 1100 cm^{-3} during winter and from 3200 to 4000 cm^{-3} during summer, representing an increase in concentration from night to day of 40–47% and 45–60% for winter and summer, respectively.

In boundary layer sites, the particle number concentrations do not always show a diurnal variation. In Finnish and Swedish remote measurement stations, an increase of concentrations is observed during the day only for nucleation event days (Tunved et al., 2003). The increase of concentrations during the day observed at the puy de Dôme station can result from nucleation events (Venzac et al., 2007), but can

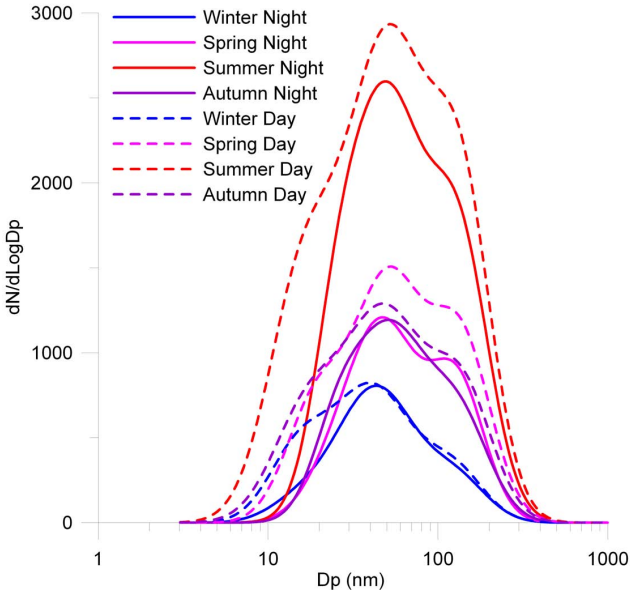

Fig. 3. Nighttime and daytime median size distribution for each season calculated over the January 2006–December 2007 period, nighttime = 00:00 to 06:00 UTC; daytime = from 06:00 to 19:00 UTC.

also result from the growth of the boundary layer over the height of the mountain top, or more intense daytime emissions during the warm season, as mentioned earlier. An increase of biogenic emissions with higher temperatures during summer would not necessarily be detected in the boundary layer because higher temperatures also lead to a higher boundary layer height in which particles are more diluted.

3.2 Size distributions

The record of aerosol size distributions at puy de Dôme spans over a shorter period (January 2006 to December 2007) but still permits to derive a seasonal variability of size-segregated aerosol concentrations. The size distributions can be split into three lognormal modes. Each lognormal mode is described by its modal median diameter (Dp), geometric standard deviation (σ) and integral number concentration (N). The SMPS data were fitted from one-hour averages, using a Labview procedure in which the modal diameters are constrained within a diameter range. The modal diameter ranges are D_p <35 nm for the nucleation mode, 35<D_p <70 for the Aitken mode, and D_p >70 nm for the accumulation mode. In the fitting procedure, the modal integral number concentrations were initialized with the integral number concentrations summed over the above mentioned size ranges. The nucleation mode cannot be well captured by our fitting procedure when the modal median diameter is close to the SMPS detection limit of 10 nm and, therefore, at the onset of new particle formation events, the size and concentrations of new particles may be misestimated.

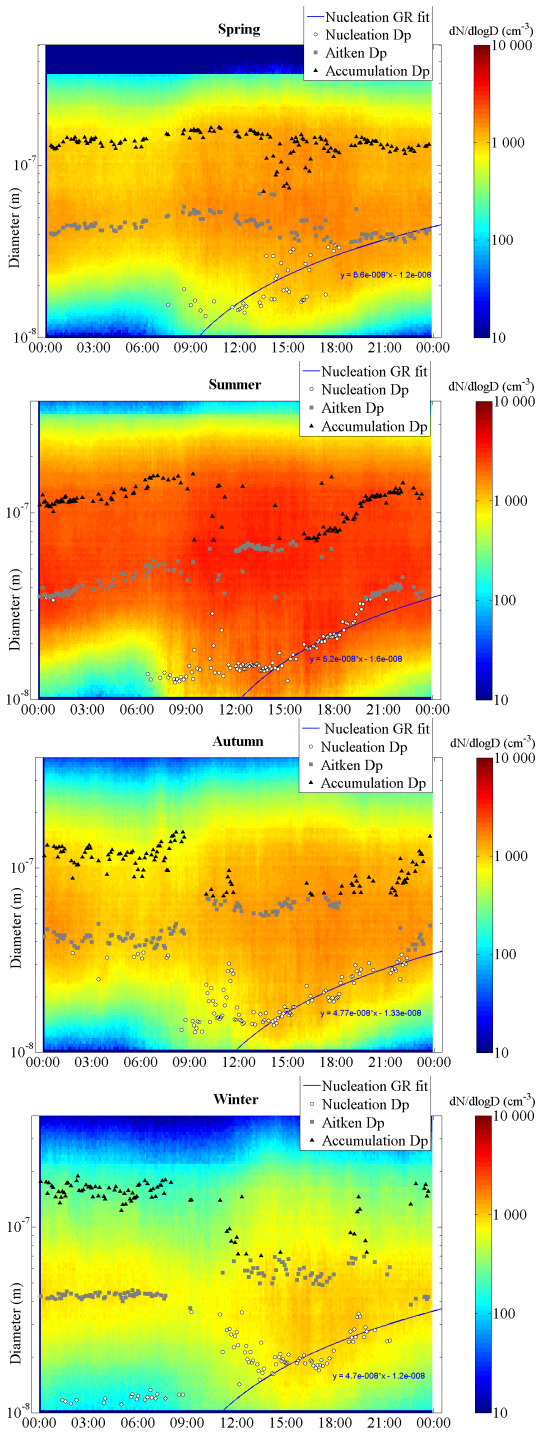

Fig. 4. Median diurnal variation of the aerosols number size distribution for each season calculated from SMPS measurements over the January 2006-december2007 period. The X axis corresponds to 00:00 UTC to 24:00 UTC, the Y axis corresponds to aerosol size (from 10 to 500 nm) and the colour bar represents the normalized concentration (dN/dLogDp). The diameter of each modes and the nucleation growth rate are also represented

.

Correlation plots between the modal integral number concentrations and the total number concentrations show that the best correlation is found for the Aitken mode integral number concentrations (R^2=0.61) which represent around half of the total number concentration over the whole year. The accumulation mode integral number concentrations are less correlated with the total number concentration (R^2=0.38) and represent 30% of the total number concentrations. The least correlated modal number concentrations are found for the nucleation mode (R^2=0.27) which accounts for 20% of the total concentrations.

The analysis of nighttime (00:00 to 06:00 UTC) and daytime (06:00 to 19:00 UTC) median size distributions for the different seasons (Fig. 3) evidences different features which are also outlined by the lognormal characteristics summarized in Table 1.

The ultrafine particles are four to five times more numerous during summer than during winter. This is consistent with more frequent nucleation events during summer compared to winter. This tendency is also observed for the Aitken and accumulation mode integral number concentrations which are both increased in summer by a factor of 3 and 6, respectively, compared to winter number concentrations. Part of this last observation is presumably due to more frequent vertical transport of pollution plumes from the boundary layer during summer. Aitken particles comprise a higher number fraction of the total particle concentration, and drive the winter to summer increase observed on the total number concentrations (with, during daytime, 1240 more particles cm^{-3} during summer compared to winter).

Diurnal variations of the size distribution can be averaged for each of the four seasons (Fig. 4). For each season, the evolution of the size distribution during a full day is structured as follows: 1-at night an Aitken mode prevails, 2-in the morning freshly formed ultrafine particles appear around 09:00 UTC, and 3-grow into the Aitken mode in the following hours. The accumulation mode integral concentrations rise in the morning as well, but later than the nucleation mode integral number concentrations. The nucleation and accumulation mode integral number concentrations are not correlated over the whole period, which shows that the new ultrafine particle formation process is not linked to the transport of pollutants (represented by the accumulation mode particles). The nucleation mode that we describe in the present paper represents an already grown nucleation mode as it is detected after particles have reached diameters larger than 10 nm. An adequate instrument (Air Ion Spectrometer, AIS) has been used to track nucleation events down to the sub-nanometer size. It shows that nucleation is observed on average on half of the measurement days, with a minimum frequency of 29% during winter (Venzac et al., 2007, and unpublished data). The solar radiation reaching the puy de Dôme station shows a significantly higher median value for nucleation event days than for non event days, indicating that nucleation seems favoured under clear sky conditions. Frequent new particle formation events has recently been observed at 5079 m a.s.l., Nepal, which may be associated to the occurrence of polluted valley air masses mixing up with free tropospheric air (Venzac et al., 2008). A more detailed description of the seasonal variation of nucleation and new particle formation events taking place at the Puy de Dôme will be described in a separate paper. New particle formation and growth is defined by the occurrence of higher concentrations of 10 nm particles at midday and their following growth of 10 nm particles to larger sizes (up to the Aitken mode size). Due to their relatively high frequency, the impact of new particle formation and growth events is detectable on the median size distribution shown in Fig. 4 for all seasons. For all seasons, the total particle concentration increase during the day compared to night observed in Sect. 3.1. is mainly due to an increase of the nucleation mode particles concentrations. This increase is highest during summer (425 more particles cm^{-3} during daytime compared to nighttime). The median growth rate of 10 nm particles which can be inferred from Fig. 4 are 5.6, 5.2, 4.8 and 4.7 nm h^{-1} for spring, summer, autumn and winter, respectively. These growth rates falls within the range of values measured in remote rural environments (Kulmala et al., 2004).

We observe that the nucleation modal median diameter ranges between 15 nm and 25 nm at night, and between 15 nm and 19 nm during the day, from winter to summer respectively. Except during winter, particles which have freshly nucleated during the day have a smaller size than the more aged nucleation mode particles observed during the night, observed with lower concentrations, due to probable coagulation processes. The aged, nighttime nucleation mode particles are larger during summer compared to winter, which is consistent with the presence of more VOCs leading to enhanced growth in summer compared to winter. The median diameter of the Aitken mode particles varies between 43 nm and 52 nm during the night (winter and summer, respectively), and between 41 nm and 51nm during the day. Hence, the Aitken and accumulation mode median diameters are also larger during summer than during winter.

These results can be compared to the aerosol size distribution seasonal analysis performed by Nyeki et al. (1998) and Weingartner et al. (1999) for the Jungfraujoch station (3580 m asl, Switzerland). Minimum particle number concentrations were also found for winter and maximum during summer. Nighttime Aitken integrated number concentrations are 270 cm^{-3} during winter compared to 455 cm^{-3} during summer, which is two (winter) to three times (summer) lower than to the puy de Dôme Aitken mode number concentrations. At the Jungfraujoch station, the Aitken mode number concentrations dominate the total number concentration, which is in agreement with our measurements. Modal median diameters found at the Jungfraujoch station are, on average over the year, very similar to the ones found in the present study. Moreover, Weingartner et al. (1999) found a seasonality of the modal median diameter of both Aitken

Table 1. Parameters resulting from the log normal fitting procedure on the average daytime (06:00 to 19:00 UTC) and nightttime (00:00 to 06:00 UTC) SMPS size distribution lognormal parameters calculated for each season from January 2006 to December 2007.

		Night			Day		
		σ	D_p (nm)	N (cm^{-3})	σ	D_p (nm)	N (cm^{-3})
Nucleation	Winter	1.5	15	50	1.5	15	180
	Spring	1.5	24	100	1.5	19	300
	Summer	1.4	25	275	1.6	16	700
	Automn	1.4	25	150	1.6	17	330
Aitken	Winter	1.7	43	460	1.7	41	460
	Spring	1.6	48	580	1.6	51	725
	Summer	1.65	50	1325	1.75	51	1700
	Automn	1.65	52	610	1.7	49	700
Accumulation	Winter	1.5	130	105	1.5	125	130
	Spring	1.45	130	325	1.5	137	460
	Summer	1.5	135	675	1.5	140	750
	Automn	1.5	135	250	1.5	130	325

and accumulation modes, with larger diameters during summer compared to winter. The accumulation mode integral number concentrations are also similar for both sites during winter, but twice as high at the puy de Dôme station during summer. This observation indicates a higher influence of the boundary layer on the accumulation mode number concentrations at puy de Dôme during summer with respect to higher altitude sites such as Jungfraujoch. Similar altitude dependency of aerosol variables is discussed by Legrand et al. (2007).

4 Links between Aerosol physical properties and the air massorigin

The observed variability of the particle concentration and size distribution at puy de Dôme may result from different processes including local dynamics and in particular: a) changes in the mixing layer height bringing more or less concentrated boundary layer air to the sampling site, b) emission intensity at the surface, c) seasonality of air mass origin advected to the site, and d) photochemical processes leading to secondary particles. We already showed that the factor (d) is playing a role in the diurnal variability with the high contribution of the nucleation mode integral concentrations to this variability. Moreover, the frequency of new particle formation events changes according to season, leading also to a seasonal variability. It is not easy to dissociate the role of each of these processes as they may be enhanced or suppressed by identical variables. For example, photochemical processes and elevation of the mixing height are both enhanced by intense radiation solar radiation. In the following section, we will study the seasonal evolution of factors (a) and (c) to provide an better description of the causes for the variability of the physical properties of long-range transported aerosols.

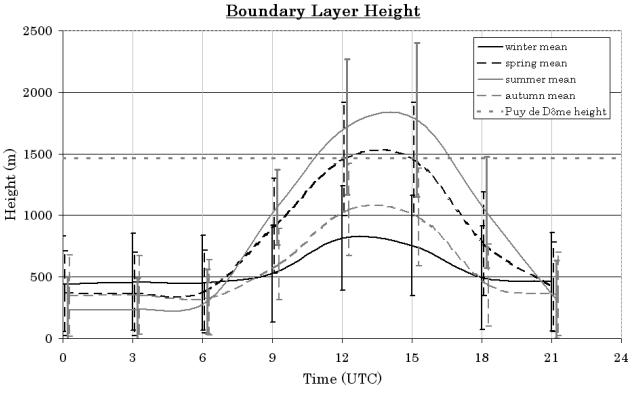

Fig. 5. Diurnal variation of the boundary layer height (computed with ECMWF for the year 2003 to 2007) averaged for the four seasons, with the variability within each season indicated as standard deviation.

4.1 Seasonality of the boundary layer air reaching the puy de Dôme

The vertical transport from the boundary layer to the puy de Dôme station can be as a first approximation derived by modelling the height of the boundary layer using ECMWF products. In Fig. 5, the 3-h average height of the boundary layer is calculated for the four seasons using 4 years of computed data, from 2003 to 2007. Boundary layer heights are derived from meteorological fields of the ECMWF IFS model (6-hourly forecast, based on 4-D-VAR analyses) (ECMWF, 2002) for the latitude and longitude of the puy de Dôme with

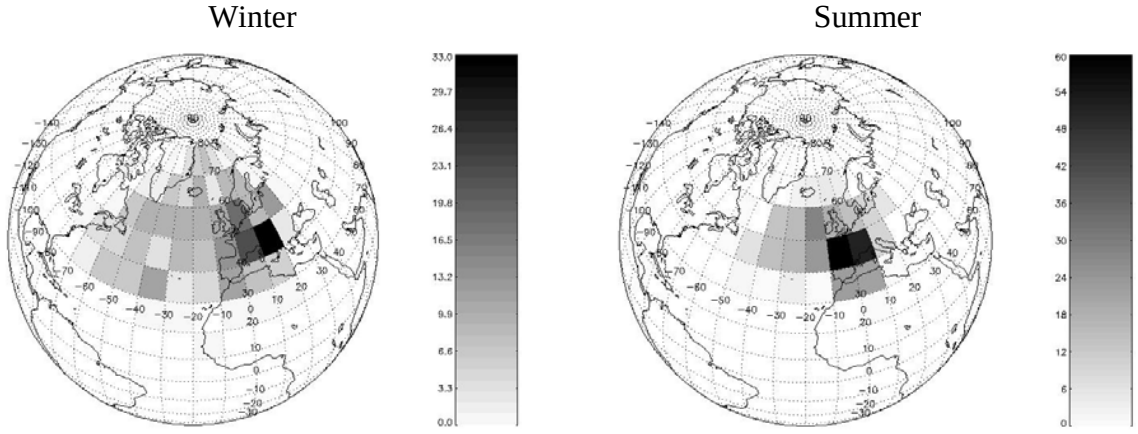

Fig. 6. Frequency distribution of three-days back trajectories arriving at the puy de Dôme station, calculated using HYSPLIT for summer and winter over the 2003–2006 period on a day-to-day basis at 00:00 UTC.

a resolution of $0.5° \times 0.5°$. Results confirm that the air reaching the puy de Dôme sampling site is strongly influenced by the BL during the day in summer, while on average, the model shows that the site lies above the boundary layer, either in the residual layer or in the free troposphere (FT), in winter. At night, the modeled BL height is lower than 500 m a.s.l. for all seasons.

However, we have to consider that the exchange between BL and FT at mountain sites is further increased by forced convection which is not properly accounted for by global forecast models. To study the possibility that the seasonal variation of aerosol concentrations observed at night can be due to a seasonal variation of forced convection, we calculated the probability for the boundary layer height computed at night to be uplifted to the height of the puy de Dôme. First, the relationship between the wind speed and atmospheric stratification can be quantified with the Froude number (F) according to Eq. (1) (Baines, 1997):

$$F = \frac{U_0}{N H} \tag{1}$$

Where U_0 is the wind speed at the height of the puy de Dôme, H the height difference between the puy de Dôme station and the foot of the mountain, and N the Brunt-Väisälä frequency calculated according to Eq. (2):

$$N = \sqrt{\frac{g}{\theta_v} \frac{\partial \theta_v}{\partial z}} \tag{2}$$

where θ_v is the virtual potential temperature and z the altitude. For unstable conditions, the boundary layer will presumably reach the height of the puy de Dôme when it encounters the obstacle. For stable conditions, a splitting height Hs can be calculated according to Eq. (3):

$$H_s = H\,(1 - F) \tag{3}$$

For an altitude lower than Hs, the flux will deviate from the obstacle while at altitudes higher than Hs it will be uplifted along the mountain slope. Hs was calculated every 3 h for the 2006 and 2007 period (over which only about 22% of the full meteorological data are available), and compared with the boundary layer height simulation. At nighttime, Hs is below the BL calculated height for 62% of the summer observation and 54% of winter observations. Hence, for a little more than half of the time, uplifting of BL air to the top of the mountain potentially takes place at night. However, no clear seasonality is observed in the calculation of Hs for nighttime hours. Still, both number concentrations and size distributions present a clear seasonal signal when only the nighttime measurements are selected (Figs. 1b and 5). We observe an increase of nighttime concentrations from winter to spring and autumn and finally summer. This increase can not be explained by a seasonal variation of the BL air influence on the puy de Dôme atmospheric concentrations but rather by a seasonal variability of the tropospheric aerosol, whether it is linked to the BL or to the residual layer/free tropospheric composition.

Hence, by selecting only the nighttime aerosol concentrations, we can exclude the source of seasonal variability due to the seasonal change in the frequency at which the BL height reaches the top of the puy de Dôme. In the following sections, we will explore the other possible causes for seasonal variability on the tropospheric aerosol concentrations by selecting nighttime concentrations.

4.2 Seasonality of air mass types reaching the puy de Dôme

In this section, we investigate the variability of air mass back trajectories according to seasons. It should first be noted that the height of the air mass back trajectory endpoints, using the HYSPLIT transport and dispersion model, does not vary with the season. The variability can, therefore, not be explained

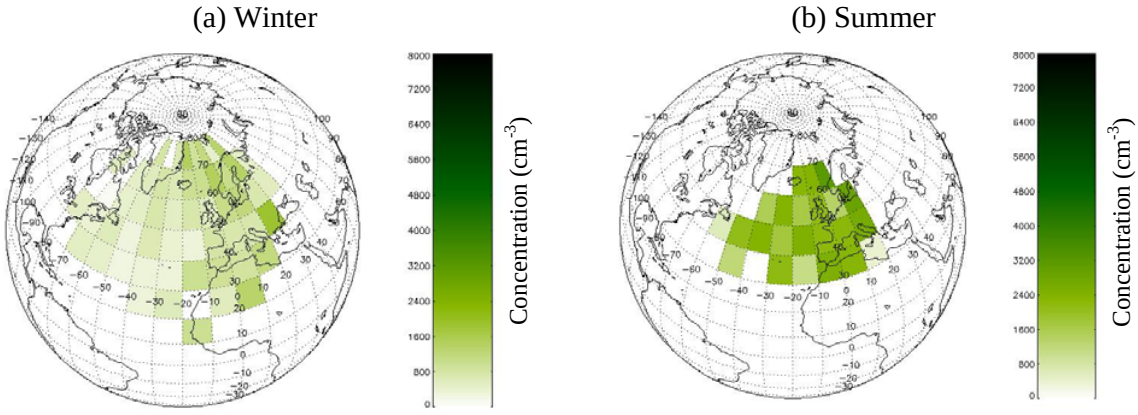

Fig. 7. Puy de Dôme median particle number concentrations during winter and summer according air masse origin (defined by trajectory path) over the 2003–2006 period.

by air masses having spent more time, on average, close to the ground. The frequency distribution of three-day back trajectories arriving at the puy de Dôme station, calculated using HYSPLIT, are mapped in Fig. 6 for summer and winter. We have discarded spring and autumn seasons for studying the causes of seasonal variability as the differences are most pronounced between summer and winter. The calculation is statistically performed over the whole 4-year measurement period with a 10° longitude per 10° latitude and a one day (midnight) resolution. We chose this type of representation rather than a sector type of air mass classification in order to take into account the time during which the air mass is transported over a continental area. Long-distance trajectory paths are associated with high wind speeds and represent air masses with a shorter lifetime over the continent.

The comparison of air mass trajectory pathways for different seasons shows that winter air masses reaching the puy de Dôme have traveled over longer distances from the west compared to summer air masses. The seasonal variation in the length of transport routes could partially explain the aerosol concentration seasonality at night. Tunved et al. (2005) observed that equivalent air masses contain very different aerosols when investigated at different stations. They argued that both formation area and transport pathways are crucial to shape the aerosol size distribution. Using our data set, we can investigate, for a given air mass trajectory path, whether a seasonal variation is still observed on the aerosol total concentrations. The goal here is to further investigate the cause of the seasonal variation of the aerosol concentration at night at the puy de Dôme station.

4.3 Nighttime seasonality of a given trajectory path

We calculated the puy de Dôme median particle number concentrations during winter and summer according to the origin of air masses (defined by trajectory path) (Fig. 7). For the same reason as stated in Sect. 4.2, we limited our investigation to winter and summer. We observe that for a given trajectory path, concentrations are significantly higher during summer than during winter. On average, at night and in marine air masses, aerosol particles are 4.4±1.8 times more concentrated during summer than during winter for a same transport route. In continental air masses, we also observe an increase of the aerosol particle concentrations by a factor of 5.8±1.3 from winter to summer. There is no latitudinal gradient in the winter to summer increase.

Hence, part of seasonality in the nighttime particle concentrations is likely due to a seasonal change in the emission sources within the troposphere/residual layer. The aerosol particle concentration integrated over the whole atmospheric column is clearly increased from winter to summer, as captured by regional chemistry models over Europe (Marmer and Langmann, 2007). Finally, enhanced secondary particle formation in the boundary layer or in the FT in summer can also feed the nighttime aerosol concentrations. In fact, the increase of total aerosol concentrations at the puy de Dôme level between winter and summer at night are driven by an increase of the nucleation and accumulation modes integral concentrations (Table 1). This confirms that one of the processes responsible for the high altitude higher concentrations during summer is new particle formation.

5 Size distributions in the free troposphere/residual layer according to air mass types

In order to provide typical aerosol size distributions of large scale relevance, the analysis is now constrained to nighttime measurements for which the splitting height Hs (Sect. 4.1.) is superior to the BL Height (Sect. 4.1.), hence to the free tropospheric/residual layer air masses. The lognormal fitting parameters of the distribution are given in Table 2 and size distributions plotted in Fig. 8 .

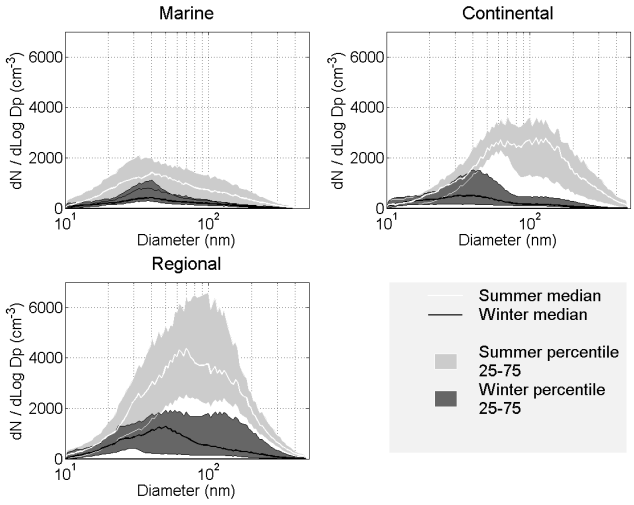

Fig. 8. Nighttime median size distribution and 25–75th percentile ranges for **(a)** marine, **(b)** continental, and **(c)** regional air masses during winter and summer. See text for the definition of marine, continental and regional air masses.

Discrimination between marine and continental air masses is arbitrarily performed on the basis of Fig. 6. Marine air masses are defined as those with 72 h air mass trajectory pathways originating further west of longitude 20° W, while continental air mass are defined as those originating further East of longitude 10° E. Trajectory pathways originating between these two longitudes and between 40° N and 50° N latitudes are characteristics of regional air masses which spent substantial amount of time over continental areas in particular over Western Europe.. During winter, advection of the three air mass types (marine, continental and regional) occur with about the same frequency (38%, 41% and 21% for marine, regional and continental, respectively) while during summer, regional air masses are more frequent and continental air masses rarer (25%, 72% and 4%, respectively).

5.1 Size distributions in marine air masses

The total concentration of marine air masses sampled at the puy de Dôme station is on average 300 cm^{-3} during winter and 1090 cm^{-3} during summer. Marine aerosol total number concentrations are dominated by the Aitken mode number concentrations, representing 56% and 59% of the total particle number in winter and summer, respectively. In these air masses, the Aitken mode median diameters are found at 39–42 nm and the accumulation median diameter at 105–120 nm, with the largest diameter found during summer as reported for the whole data set.

The puy de Dôme marine aerosol sizes and concentrations can be compared to those with clean marine aerosols sampled at the Mace Head research station, Ireland. While number concentration in winter are similar, concentration in summer is two time higher at puy de Dôme as respect to Mace Head (Yoon et al., 2007). This indicates that air masses originating from the Atlantic Ocean acquire more continental characteristics over land, even if transport takes place at high altitude. This continental impact is however reduced in winter for which the air mass conserves a very strong marine signature. In that case, aerosols sampled at 1465 m a.s.l. in air masses of marine origin are not significantly different from aerosols sampled directly in the marine boundary layer from which they may have been transported at higher altitudes. Modification of marine air masses over land is also observed by Birmili et al. (2001) at a BL site in central Germany where marine air masses had acquired strong continental characteristics during their transport over the continent. Birmili et al. (2001) measured in these air masses an aerosol concentration of 2300 cm^{-3} in the Aitken mode and 500 cm^{-3} in the accumulation mode. Marine air masses sampled during autumn at Hyytiälä also contained median particle concentrations on the order of 2000 cm^{-3}, excluding the nucleation mode (Tunved et al., 2003), which is significantly higher than concentrations usually measured at coastal sites. Aerosol concentrations at Coastal stations reported by Tunved et al.,(2005) are similar to those found in this work (Tunved et al., 2005). A comparison with particle size distributions sampled at Monte Cimone (Northern Italy) originating from the Mediterranean sea sectors shows that Aitken mode particles are four times more concentrated and almost two times larger than the puy de Dôme aerosols in marine air masses (Van Dingenen et al., 2005). The concentrations and size of aerosols sampled at the puy de Dôme in marine air masses are actually closer to those sampled at the Monte Cimone in free tropospheric air masses than to those sampled in marine air masses, as classified by Van Dingenen et al. (2005). The question is whether the definition of "free troposphere" type of aerosols is sufficient as a global classification, or if this type should be further subdivided into "free troposphere-marine", and "free troposphere-continental" aerosol.

5.2 Size distributions in continental air masses

The total concentration in continental air masses sampled at the puy de Dôme station is on average 375 cm^{-3} during winter and 2285 cm^{-3} during summer. The nucleation and Aitken mode integral number concentrations are of the same order of magnitude as in marine air masses for all seasons. These concentrations are significantly lower than those given by Whitby (1978) for Aitken mode particles for continental aerosols (6400 cm^{-3}). The major difference between marine and continental air masses is found in the accumulation mode integral number concentrations during summer. About half of the total aerosol concentration is found in the accumulation mode in continental air masses during summer. Tunved et al. (2005) already observed an increase in Aitken and accumulation mode number concentrations with increasing continental influence. The Aitken and accumulation mode integral

Table 2. Free tropospheric/residual layer nighttime size distribution lognormal parameters for marine, continental and regional air masses under summer and winter conditions calculated on the SMPS one-hour average SMPS size distributions from January 2006 to December 2007.

		Winter			Summer		
		σ	D_p (nm)	N (cm^{-3})	σ	D_p (nm)	N (cm^{-3})
Marine	Nucleation	1.5	16	50	1.4	20	130
	Aitken	1.5	39	170	1.6	42	650
	Accumulation	1.55	105	80	1.6	120	270
Continental	Nucleation	1.4	16	80	1.5	24	235
	Aitken	1.55	37	230	1.5	58	875
	Accumulation	1.5	125	65	1.6	140	1175
Regional	Nucleation	1.45	22	150	1.5	28	500
	Aitken	1.5	49	530	1.5	61	1650
	Accumulation	1.5	140	150	1.5	145	1200

concentrations in continental air masses are lower than those given by Whitby (1978) but larger than those observed at Hyytiälä during summer, (Mäkelä et al., 2000). In agreement with Tunved et al. (2003) at the Hyytiälä remote boreal forest station, the summer Aitken mode median diameter is shifted toward larger sizes (37 nm in winter and 58 nm in summer), as reported for the whole data set.

Our results compare well to those of aerosols sampled in the remote boreal forest both in terms of concentration and size, except for 1) the nucleation mode, partly because we selected nighttime measurements and 2) for higher accumulation mode summer concentrations at the puy de Dôme. The puy de Dôme summer continental aerosol also compares very well to Eastern Europe air masses sampled during summer at the Monte Cimone station (Van Dingenen et al., 2005). As a result, it appears that the air masses sampled at the puy de Dôme, the boreal forest (Hyytiälä), or the Monte Cimone for Eastern sectors have similar characteristics, which would be inherent to background continental air masses.

5.3 Size distributions in regional air masses

Aerosols sampled within regional air masses show higher concentrations compared to those sampled in continental air masses both for the winter ($830\,cm^{-3}$) and summer ($3350\,cm^{-3}$) seasons. Basically, all modal integral concentrations are doubled in regional air masses compared to continental air masses, except for the accumulation mode number concentrations which are similar in both air mass types. Moreover, particles in the regional air masses are larger compared to particles sampled in marine and continental air masses, and 75th percentile concentrations reach higher values than in continental air masses in winter. This can potentially be due to longer residence times above anthropogenic source areas along such as the UK, Benelux, Germany, Northern France down to Spain and the Marseille/Genoa area. In terms of size and concentrations, aerosol size distributions observed at the puy de Dôme station in regional air masses are comparable to those sampled in west-European or east-European sector air masses at the Monte Cimone station during summer (Van Dingenen et al., 2005). These aerosols may be representative of 1–2 day aged anthropogenic particles mixed with background FT/residual aerosols.

Overall, the number concentrations derived for the free troposphere/residual layer are significantly lower than those discussed before data reduction for all air masses except for regional air masses. Actually, the marked seasonal variation observed on the total data set mainly seems to be attributed to the regional air masses. This can be explained by the frequent high particle concentrations in regional air masses. However, seasonal changes are still observed for all air mass types. Summer modal integral number concentrations are increased by a factor of 3 compared to winter for all air mass types and modes, except for the continental and regional air masses accumulation modes which are increased by a factor of 18 and 8, respectively. Again, this can be due to both seasonal changes in the air mass origin from winter to summer as described in Sect. 4.2. and enhanced particle concentrations in the residual layer/free troposphere in summer. The latter observation may be explained by higher emission intensity in the boundary layer during summer, stronger exchanges between the boundary layer and the free troposphere, as well as by enhanced photochemical processes.

6 Summary and conclusions

Five years of integrated aerosol concentrations and two years of aerosol size distributions sampled from the puy de Dôme mountain site have been analyzed in order to provide an air mass-based climatology of aerosol properties. Total

concentrations were inferred from a CPC 3010 with a size cut of 10 nm, while size distributions were calculated from SMPS measurements over the 10 to 500 nm size range. We observed a strong seasonality with maximum number concentrations during summer and minimum number concentrations during winter. This variability results from various processes acting at different temporal scales which are studied separately. Concentrations show a clear diurnal variation with a maximum during daytime and minimum during nighttime. The diurnal increase is first attributed to the BL height development during the day which reaches the height of the puy de Dôme more frequently during the warm seasons and may partly explain the seasonal variability in the daily aerosol concentrations. Second, the diurnal increase can be attributed to frequent new particle events. At the puy de Dôme, a nucleation mode with a geometric median diameter at 15–16 nm appears at midday and is observed to grow in size during the night at all seasons. An increase in the number concentration from winter to summer is found for each mode but particularly for the Aitken mode. We also found a winter to summer increase in the particle median diameter in all modes, presumably attributed to higher concentrations of condensable gazes during summer.

At night (00:00–06:00), the median hourly total concentration varies from 600 to 800 cm^{-3} during winter and from 1700 to 2200 cm^{-3} during summer. At the puy de Dôme, the seasonal variations of the nighttime aerosols appear to be independent of the seasonal variations of the nightime BL height. We observed that the seasonal change in the nighttime concentration is partly due to a seasonal variability in the transport routes. The air masses reaching the puy de Dôme experience shorter residence times over the continent during winter compared to summer. But we also found that for a given transport route, nighttime aerosol particles are more concentrated during summer compared to winter. Thus, other factors than the trajectory path seasonal variability are responsible for the seasonality in the nighttime concentrations.

The residual layer/free troposphere nighttime samples were selected from our data set and further segregated into marine, continental or regional air mass types. Aerosol size distributions are not very different when sampled in marine air masses or in continental air masses, except for a drastic summer increase of the accumulation mode number concentrations in continental air masses. On average, the aerosol size distributions sampled at the puy de Dôme in marine air masses compare well with those reported in the literature for the clean marine boundary layer, but this remains to be confirmed by chemical analysis. Aerosol size distributions sampled at the puy de Dôme in marine air masses are also very similar to those sampled in free tropospheric air masses as classified by Van Dingenen et al. (2005). In continental air masses, the aerosol size distribution sampled at the puy de Dôme compare well to those reported by Tunved et al. (2003) in the boundary layer and by Van Dingenen et al. (2005) at the Monte Cimone station in western and eastern European air masses during summer. Again, a chemical analysis would help to improve our understanding of the similarities between the puy de Dôme aerosol particles and aerosol particles at other background sites.

After data reduction, we found that the aerosol number concentrations are still significantly higher during summer than winter, which can be due to both seasonal changes in the air mass origin from winter to summer and enhanced concentrations of particles in the residual layer/free troposphere in summer. Latter observation may be explained by increased emission intensity in the boundary layer during summer associated with stronger exchanges between the boundary layer and the free troposphere, as well as by enhanced photochemical processes. The seasonal variability in aerosol sources seems to be predominant over the continent compared to the seasonal variation of marine aerosol sources. This enhanced seasonal variability over the continent is mainly found for the accumulation mode particles. We believe that the seasonal dependence of the number concentration and size distribution for different air masses can be extrapolated to the regional scale and, therefore, used as input to transport models.

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