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Seasonal variation of aerosol size distribution at Puy de Dôme (1465 m a.s.l., central France)

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Abstract

Particle number concentration and size distribution are amongst the most important variables needed to constrain the role of the atmospheric particles in the Earth radiative budget. 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 where the occurrence of aerosol in elevated layers cannot be resolved from most instruments in space. Therefore it is crucial to provide ground based measurements of suited aerosol variables to obtain closure between all independent information sources. In this paper, we investigate diurnal and seasonal variability of aerosol number concentration and size distribution at the Puy de Dôme research station (France, 1465 m a.s.l.). We report variability of aerosol particle total number concentration measured over a five years (2003–2007) period and aerosol size distributions over a one year period (January to December 2006). 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 from 2500 to 3500 cm^{-3} during summer. An averaged size distribution of particles (10–500 nm) was calculated for each season. A variability in the size of aerosols sampled at the Puy de Dôme is also observed on the seasonal and diurnal basis. Because the site lies 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 free tropospheric conditions only. We show that the variability is due to both seasonal changes in air mass origin from winter to summer and enhanced concentration of the free troposphere in summer. The later observation can be explained by higher emission intensity in the boundary layer, stronger exchange between the boundary layer and the free troposphere as well as enhanced photochemical processes. Finally, aerosol mean size

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distributions are calculated for a given air mass type (marine/continental/regional) according to the season, for the specific conditions of the free troposphere. These results are of regional relevance and can be used to constrain chemical-transport models over Western Europe.

1 Introduction

Seasonal and diurnal variation of aerosol parameters such as $PM_{2.5}$ and PM_{10} mass concentration have been extensively documented in various environments (Van Dingenen 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 concentration and size distribution. This is an important limitation because these variables are amongst the most relevant to constrain the role of the atmospheric particles in the Earth radiative budget. Important parameters such as the scattering coefficients are indeed 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 investigate processes involved in particle formation and sinks.

Particle number concentration and size distribution are also linked to 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 (Dp) <1 μm) and specially ultrafine (Dp<0.1 μm) fractions. Because of the two competing processes of homogeneous nucleation and growth of particles by condensation of gas-phase species onto pre-existing particle, 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) rural and remote sites (Birmili et al., 2001; Mäkelä et al., 2000; Tunved et al., 2003; Rodriguez et al., 2005), artic atmosphere (Komppula et al., 2003), marine environments (Satheesh et al., 2006; Yoon et al., 2006) and the free troposphere (Raes et al., 1997; Weingartner et al., 1999)

Current knowledge of aerosols number size distributions has generally identified the number size distribution to be composed of a Nucleation mode (10–20 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 by inputs of additional sources, or dilution, deposition and coagulation processes within 36 h 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 also show maximum concentrations during winter due to an accumulation during the night of accumulation mode particles in a low boundary layer height (Rodriguez et al., 2005), and others maximum concentrations during spring due to a maximal frequency of nucleation events (Komppula et al., 2003; Tunved et al., 2003). Hence, for climate modelling to use inputs as realistic as possible, 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. First, because continuous measurements of fine aerosol size distributions and number concentration from elevated sites are scarse in Europe (Nyeki et al., 1998; Weingartner et al., 1999), and second, because mountain site are often influenced by long-range transport rather than local sources, and, hence, provide information on aerosol variability at the regional scale. In this paper, we report diurnal and seasonal variability of aerosol particle total number concentration measured over a six years (2002–2007) period and measurements of aerosol size distributions measured over a one year period (January to December 2006).

2 Sampling techniques and site

The Puy de Dôme research station is located at 1465 m above the sea level in Central France (45°46′ N, 2°57′ E). The station is surrounded mainly 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. Meteorological parameters, including the 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 monitored continuously throughout the year. Winter temperatures vary typically from −5 to +1°C, summer temperatures from 10 to 20°C. Westerly winds are dominant. During the November–April period, the road access to the station is restricted to experimental work while it is opened to public transport during the rest of the year. In any case, traffic is stopped 500 m away from the sampling station and does not influence sampled air composition. In fact, CO and NO_x concentrations are higher during the November–April period than during 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-cloud, the aerosol

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sampling is performed through a whole air inlet (WAI) which ensures efficient sampling of both cloud droplets and interstitial aerosol in the presence of clouds. Wind speed is decreased in the vicinity of the WAI by a series of metallic fences ensuring efficient sampling even at elevated wind speed. Based upon theoretical considerations, the WAI is capable of efficiently sampling droplets <35 μm for wind-speed <10 m s^{-1}. During cloudy conditions, interstitial aerosols and evaporated cloud residues are sampled simultaneously at a relative humidity close to 50%. Total aerosol concentrations were measured from 2002 to 2005 and 2007 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 lack of data during the first half of 2003 and 2005.

From January to December 2006 a SMPS (Scanning Mobility Particle Sizer) monitored the particle number size distribution (10–500 nm) through the WAI. The SMPS comprised a TSI Inc. 3010 Condensation Particle Counter (CPC) and a custom-made Differential Mobility Analyzer (DMA) (Villani et al., 2007) and is operated continuously with a two-minute time resolution. Data quality of the size-distribution was first checked by comparison of the integrated SMPS number concentration with concentration measured by an additional TSI Inc. 3010 CPC connected to the same sampling line over limited periods, second by an inter-calibration procedure within the EUSAAR project (www.eusaar.net). During this last exercise, the number concentration agreed within 15% with a reference SMPS instrument while size determination was in agreement with the mean size measured by the reference instrument within 20% for the 20 nm particles and 10% for the 100 nm particles.

In the framework of the present paper, the number concentration is therefore derived from direct CPC 3010 measurements from 2002 to 2005 and for 2007 and from integrated SMPS measurements for the whole year 2006. However, the size distribution analysis discussed in this paper has been limited to the January 2006 to December 2006 period.

Air mass three-day back trajectories were calculated using the HYSPLIT trans-

port 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 h.

3 Seasonal and diurnal variability of aerosol number concentration and size distribution

3.1 Particle number concentrations

Monthly median number particle concentrations were calculated from the TSI 3010 CPC five-minute data acquisition, in order to have a clear picture of the concentrations long term variability (Fig. 1). We observe a clear seasonal variation over six years with a maximum during summer and a minimum during winter. The average daily aerosol concentration is 2500 cm^{-3} and 900 cm^{-3} in summer and winter, respectively. The total carbonaceous mass 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., 2003; Nyeki et al., 1998; Weingartner et al., 1999; Osada et al., 2003; Van Dingenen et al., 2005) with maxima differing according to the site. Comparing 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 and those measured at the boundary layer site of Aspvreten in Sweden. No systematic seasonal variation was observed by Van Dingenen et al. (2004) for all European sites, showing that the combination between the sources strength, dilution due to the boundary layer height and sink by precipitations impose very different features amongst European sites.

The variability of aerosol number concentration is also resulting from changes occurring on time scale of a day. The diurnal variability of the median has been calculated for four different seasons corresponding to the maximum concentration (June/July/August: summer), the minimum concen-

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trations (December/January/February: winter) and intermediate concentrations (March/April/May: spring; September/October/November: autumn) and plotted in Fig. 2.

The diurnal variation of the median number concentration shows high values between 12:00 and 18:00 UTC during summer and winter. 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 is in the range of 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.

Boundary layer sites do not always show a diurnal variation of the particle concentration. 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 also be resulting from the advection of air from surface layers due to the horizontal variability of boundary layer height during daytime.

3.2 Size distributions

The record of aerosol size distribution at Puy de Dôme spans over a shorter period (January to December 2006) with respect to that of the number concentration. It permits, however, to derive the seasonal variability of the size distribution. Analysis of the median diurnal variation of the size distribution for the 4 seasons indicates little season-to-season size variability featuring: Aitken particles with a mode around 50 nm and accumulation particles with mode around 150 nm (Fig. 3). The background signal is modified by freshly formed ultrafine particles appearing from 06:00 UTC in summer and 12:00 UTC in winter, growing into the Aitken mode in the following hours. The occurrence of nucleation events at the Puy de Dôme has already been partly addressed by Venzac et al. (2007). Due to their relatively high frequency, the impact of nucleation

events is detectable on the median size distribution for all seasons although it does not occur on a daily basis.

Analysis of Nighttime (00:00 to 06:00 UTC) and day time (06:00 to 19:00 UTC) median size distributions for the different seasons shown in Fig. 4, evidences different features that can be outlined when decomposing the size distribution into three lognormal modes (Fig. 4). Each lognormal mode is described by its modal diameter (Dp_N), modal standard deviation (σ) and concentration (N).

The modal standard deviation does not vary significantly according to the season nor day/night period, it varies between 1.4 and 1.7. We observe that the nucleation modal diameter ranges at night from 21 nm in winter to 27 nm in summer, while it is rather stable through the year around 19 nm during the day. Particles which have freshly nucleated during the day have a smaller size than the more aged nucleated particles which continue to be observed during the night, although in lower concentrations, due to probable coagulation processes. The aged nucleated particles are larger during summer compared to winter, which is consistent with the presence of more VOCs leading to enhanced growth in summer as respect to winter.

Seasonal changes are more easily observed by comparing the relative amplitude of each mode for winter and summer conditions (Fig. 5). The ultrafine particles are three times more numerous during summer than during winter. This is consistent with more nucleation events during summer compared to winter. Aitken particles comprise the higher number fraction of the total particle concentration (51% for the summer and 70% for the winter at night and 42% and 62% for summer and winter respectively during the day). The mode of Aitken particles is constant at 54–55 nm, at all time scales. The concentrations are not significantly different from night to day, neither from spring to autumn, but the winter concentrations are twice as low as in spring–summer–autumn.

At last, the accumulation particles are found with a mode between 135 nm and 145 nm and their concentration as well as their contribution to the total particle number is maximum in summer and minimum in winter.

These results can be compared to the aerosol size distribution seasonal analysis per-

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formed by Nyeki et al. (1998) and Weingartner et al. (1999) for the Jungfraujoch station (3580 m a.s.l., Switzerland). Minimum particle number concentrations were also found for winter and maximum during summer. Nighttime concentrations are 270 cm^{-3} during winter against 455 cm^{-3} during summer for the Aitken mode, which is dominating the number concentration, in agreement with our measurements. Modal diameters found at the Jungfraujoch station are, on average over the year, very similar to the ones found in this study. However, Weingartner et al. (1999) found a seasonality of the modal diameter of both modes, which exhibited larger diameters during summer compared to winter. The accumulation mode 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 at Puy de Dôme during summer as respect to higher 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 mass origin

The observed variability of the particle concentration and size distribution at Puy de Dôme results from different processes including local dynamics and in particular changes in the mixing layer height bringing more or less concentrated boundary layer air to the sampling site depending on emission intensity at the surface, seasonality of air mass origin advected to the site, and photochemical processes leading to secondary particles. In addition, the frequency of new particle formation events changes according to season leading to both seasonal and diurnal 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. These local/Regional processes are therefore greatly influencing the particle signal resulting in complexity to derive average size distribution that can be extrapolated for long-range transported aerosol. In the following, additional data reduction is applied to the data set

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to better understand the causes for its variability and provide an accurate description of the variability and the physical properties of long-range transported aerosols.

4.1 Influence of the boundary layer air

The vertical transport from the boundary layer to the Puy de Dôme station can be on a first approximation derived by modeling the height of the boundary layer using ECMWF.

In Fig. 6, the average height of the boundary layer is calculated for the 4 seasons using 4 years of computed data, from 2003 to 2006. Data are extracted from ECMWF for the latitude and longitude of the Puy de Dôme, with a resolution of $0.5^{\circ} \times 0.5^{\circ}$. Results confirm that the air reaching the Puy de Dôme sampling site is strongly influenced by the BL during the day during summer, while, on average, the model shows that the site lies in the free troposphere (FT) during winter. At night, the modeled BL height is lower than 500 m a.s.l. for all seasons. Hence, information on the free tropospheric aerosol representative of the free troposphere can be derived at Puy de Dôme by selecting the nighttime measurements only.

However, we have to consider that, at mountain sites, the exchange between BL and FT 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):

$$F = \frac{U_0}{NH} \tag{1}$$

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 Brünt-Vaisala

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frequency calculated according to Eq. (2):

$$N = \sqrt{\frac{g}{\theta_v}\frac{\partial \theta_v}{\partial z}} \quad (2)$$

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, the height of splitting H_s between two regimes can be calculated according to Eq. (3):

$$H_s = H\,(1-F) \quad (3)$$

if H_s is higher than H the flux will deviate from the obstacle while if H_s is lower than H it will be uplifted along the mountain slope. H_s was calculated every 3 h for the 2006 period, and compared with the boundary layer height simulation. At nighttime, H_s is below the BL calculated height for 36% of summer and 39% of winter observations, respectively implying that, uplifting of BL air to the top of the mountain potentially takes place (calculated over 50% of the one-year period, 2006, for which data are available). However, no seasonality is observed in the calculation of H_s for nighttime hours. We can therefore conclude that, although a contribution from BL air cannot be excluded during the nighttime hours, the majority of air mass vertical trajectories are expected to deviate around the Puy de Dôme mountain at night. In addition, the bias introduced by considering all nighttime measurements in the following calculation is not seasonal dependent. Obviously, it should be kept in mind that, although subsequent data analyses are performed with nighttime measurements only, the aerosol population may have been subject to photochemical processes during transport prior to sampling at Puy de Dôme.

Both number concentration and size distribution still present a clear seasonal signal when only the nighttime measurements are selected. We observe an increase of nighttime concentrations from winter to spring and autumn and finally summer, that can neither be explained by transport from the BL nor by seasonal dependency of the

nucleation process but rather by seasonal variability of the free tropospheric aerosol sampled at the station.

4.2 Seasonality of air mass types reaching the Puy de Dôme

The observed variability of aerosol size distributions at night is, at this stage, either linked to the variability of emission sources or to the variability of the source areas influencing the air at the Puy de Dôme. In this section, we investigate the variability of air mass back-trajectories according to seasons. Three-days back trajectories endpoints number density calculated using the HYSPLIT transport and dispersion model are plotted in Fig. 7. The calculation is statistically performed over the whole 4-year measurement period by attributing a 10° Longitude per 10° latitude endpoint area for each day at midnight. The number of back trajectories ending in a specific 10°×10° area is represented in Fig. 7 for summer and winter. 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. Back trajectories ending at a long distance from our measurement site have been transported by high wind speed and hence have had a short lifetime over the continent. For clarity reasons, spring and autumn seasons are at this point discarded when studying the seasonal variability causes, because they have always been intermediate between summer and winter.

The comparison of air mass trajectories density 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. It is then possible that air masses have spent more time over land during summer than during winter, which would explain the higher concentrations observed during summer compared to winter. 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. It is difficult at this stage to determine whether spending more time over land equals traveling a larger distance

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over land for an air mass. It should be noted that the height of the air mass back trajectories endpoint does not vary with the season. The variability cannot therefore be explained by air masses spending more time on average close to the ground. The seasonal variation in the length of transport routes could partially explain the aerosol concentration seasonality at night. Whether this parameter is driving the aerosol size distribution, or not, can be further investigated by studying the seasonal variation of aerosol size distributions for a given transport route.

4.3 Influence of the transport route on aerosol concentration

In this section, the objective is to investigate the aerosol variability along a given transport route for different seasons to further constrain factors driving the seasonality of aerosol concentration and size observed at the Puy de Dôme station.

We calculated the median particle number concentrations attributed to a given air mass back trajectory endpoint for each $10^{\circ}\times10^{\circ}$ section area both for winter and summer (Fig. 8). For the same reason as in Sect. 4.2, we limited our investigation to winter and summer.

Comparison of each $10^{\circ}\times10^{\circ}$ section in winter and summer shows that concentrations are significantly higher during summer than during winter. Hence, for the same transport route, a seasonal variation in the particle concentrations is observed. On average, at night, marine air masses are 3.7±1.8 times more concentrated during summer than during winter for a same air mass back trajectory ending point. For continental air masses, we also observe an increase by a factor 2.4±0.6 between winter and summer. Considering the observed summer/winter variability, no difference can be drawn between marine and continental air masses regarding the increase of concentrations between winter and summer. There is no latitudinal gradient in the winter to summer increase.

Hence, part of the change in particle concentrations between winter and summer is likely due to a seasonal change in the free tropospheric concentration. This observation can be the result of more frequent inputs from the boundary layer to the FT due

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to instabilities and turbulences along the air mass trajectories and a resulting increase of the particle number concentration in the entrainment layer. In addition to the previous process, higher emission at the surface during summer as respect to winter can contribute to this difference. The total aerosol column load 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 processes increasing the most the nighttime particle concentrations in the free troposphere are mainly increasing the nucleation and accumulation modes (Fig. 5).

As a result, we can, from this work, provide typical aerosol size distribution in the free troposphere according to air mass type (Marine/Continental/Regional) and seasons.

5 Seasonal variation of the free tropospheric aerosol size distribution

Discrimination between marine and continental is arbitrarily performed on the basis of Fig. 8. Marine air masses are defined as those with 72 h air mass back trajectory ending at longitudes lower than 20° E, while continental air mass are defined as those hours air mass back trajectory ending at longitudes higher than 10° W. Trajectories that end between these two longitudes are typical for lower wind speed or mixed air masses (marine or continental air masses spending longer periods over high density of population zones). They are representative of a more local/regional impact on the aerosol size distributions measured at the Puy de Dôme station. They will be studied separately from the marine and continental air masses and defined as regional air masses. During winter, all air mass types occur with about the same frequency (38%, 41% and 21% respectively for marine, regional and continental) while during summer regional air masses are more frequent and continental air masses rarer (respectively 25%, 72% and 4%). The analysis is constrained to nighttime measurements only.

The average size distributions for winter and summer conditions for the 3 air mass types are fitted with 3 log-normal distributions representing ultrafine, Aitken and accu-

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mulation mode particles. The characteristic parameters of the distribution are given in Table 1 and plotted in Fig. 9

The number concentration derived using the nighttime measurements only are significantly lower than those discussed before data reduction. They can be however extrapolated to the regional scale as the local BL contribution is limited. We recommend performing similar analysis to measurements performed at mountain sites in order to improve the intercomparability of data sets.

We can go further into the analysis of the results by discussing each air mass type separately.

5.1 Marine air masses

The total concentration of marine air masses sampled at the Puy de Dôme station is on average 295 cm^{-3} during winter and 645 cm^{-3} during summer. Marine aerosols are dominated by the Aitken mode, representing 88 and 84% of the total particle number in winter and summer respectively. For these air masses, modal diameters are found at 32–36 nm for the Aitken particles and 120–135 nm for the accumulation particles, regardless of the seasons. Therefore, while Aitken and accumulation particles concentration increase during summer compared to winter, the modal diameters do not show any significant change from winter to summer. This can be compared to similar measurements performed at the coastal site of Mace head, Ireland, where marine air masses have modal diameters at 31 nm for the Aitken particles and 103 nm for accumulation particle during winter time and 49 nm and 177 nm respectively for summer, with total concentrations of 253 cm^{-3} during winter and 469 cm^{-3} during summer (Yoon et al., 2007).

The Puy de Dôme marine aerosol sizes and concentrations are hence in good agreement with clean marine aerosols sampled at the Mace Head research station, Ireland, although during summer, the particles sampled at the Puy de Dôme are slightly smaller than the ones sampled at Mace Head. It could indicate that aerosols sampled at 1465 m a.s.l. in air masses of marine origin are not significantly different from the

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aerosols sampled directly in the marine boundary layer. This is contrary to the observation from Birmili et al. (2001), in which marine air masses advected to a central Germany BL site had acquired strong continental characteristics during their transport over the continent. Birmili et al. (2001) measured in these air masses an Aitken mode concentration of 2300 cm^{-3} and 500 cm^{-3} in the accumulation mode. Marine air masses sampled at Hyytiälä also contained during autumn median particle concentrations of 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. Concentrations reported at stations closer to the coast show, however, concentrations which are closer to the ones found in this work (Tunved et al., 2005). Comparison with particle size distribution sampled at Monte Cimone (Northern Italy) originating from the Mediterranean sea sectors show that Aitken mode particles are 4 times more concentrated and two times larger than the marine Puy de Dôme aerosols (Van Dingenen et al., 2005). The concentrations and size of aerosols sampled at the Puy de Dôme in marine air masses are in fact closer to the concentrations and size of aerosols sampled at the Monte Cimone in air masses classified by Van Dingenen et al. (2005) as free tropospheric than to the ones sampled in air masses classified as marine. There is a question here whether the "free troposphere" type of aerosols stands alone as a global classification, or if it should be subdivided into "free troposphere-marine", and "free troposphere-continental".

5.2 Continental air masses

The total concentration in continental air masses sampled at the Puy de Dôme station is on average 495 cm^{-3} during winter and 1825 cm^{-3} during summer during nighttime. As for marine air masses, the size distribution is again dominated by Aitken particles representing 54% (265 cm^{-3}) of the total particle number concentration in winter and 55% (1000 cm^{-3}) in summer. The Aitken mode concentrations are the same order of magnitude than the marine Aitken mode during winter, but twice the marine concentrations during summer. However, these concentrations are significantly lower than

those given by Whitby (1978) for Aitken particles for continental aerosol (6400 cm^{-3}). In agreement with Tunved et al. (2003) for the Hyytiälä station, the Aitken mode modal diameter is shifted toward larger sizes (55 nm in winter and 45 nm in summer) compared to the marine aerosols.

While marine aerosols did not show large concentrations in the accumulation mode at the Puy de Dôme, about half the concentration of continental aerosols are in the accumulation mode during summer. The Puy de Dôme continental air masses accumulation mode concentrations are again much lower than the ones given by Whitby (1978) (a mean 2300 cm^{-3}). The Puy de Dôme summer concentrations of the accumulation mode are twice as large as the ones observed in the remote boreal forest, while the winter concentrations are the same in both environments (Mäkelä et al., 2000).

These values compare well, both in terms of concentration and size distribution to aerosols sampled in the remote boreal forest, excepted for the nucleation mode, partly because we selected nighttime measurements. The Puy de Dôme summer continental aerosol also compares very well to Eastern europe air masses sampled during summer at the Monte Cimone (Van Dingenen et al., 2005). This result would indicate that the air masses sampled at the Puy de Dôme, in the boreal forest and at the Monte Cimone for Eastern sectors have the same characteristics which would be inherent to the background continental air masses.

5.3 Regional air masses

Regional air masses are selected as originating at longitudes comprised between longitudes 20° E and 10° W over the 3-days back trajectories. Aerosols sampled within regional air masses show very similar concentrations to the ones of continental air masses both for winter (550 cm^{-3}) and summer (1797 cm^{-3}) seasons. The Aitken mode is still dominant with 75% and 57% of the total number concentrations for winter and summer respectively. However, particles are larger compared to marine and continental air masses and 75 percentile concentrations reach higher values than for

continental air masses in winter, potentially indicating the influence of longer residence time above anthropogenic source areas along the transect from Benelux, Germany, the UK, northern France down to Spain and the Marseille/Genova area. Size distributions observed at the Puy de Dôme station for regional air masses are comparable in term of size and concentration to the west-european sector air masses sampled at the Monte Cimone station during summer, if the daytime concentrations are included in the Puy de Dôme calculation to fit the data set from Van Dingenen et al. (2005). This aerosol may be representative of 1–2 day aged anthropogenic particles mixed with the background FT aerosol.

6 Summary and conclusions

Five years data of total aerosol concentrations and one year data of aerosol size distributions from the mountain site of Puy de Dôme have been analyzed in order to provide an air mass based climatology of the aerosol properties. Concentrations show a strong seasonality with maxima during summer and minima during winter caused by various processes acting at different scales. Advection of air from surface layers due to the horizontal variability of boundary layer height during daytime is strongly influencing the mountain top signal, especially during the warm seasons between 12:00 and 18:00 LT. Frequent episodes of new particle formation occurring during the day, also contribute to enhancing diurnal variability of both aerosol number and size. The nighttime air masses sampled at the Puy de Dôme are most frequently representative of the free troposphere, independently of the season. It was found that the seasonal variation of the nighttime concentration was not due to a seasonal change in the vertical mixing, as observed for the daytime concentrations. In order to provide information on aerosol physical properties that can be extrapolated to the free troposphere, we reduced our analysis to nighttime measurements.

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. The seasonal

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change in the nighttime concentration is partly due to a seasonal variability in the transport routes, the air masses coming to the Puy de Dôme being transported from further away during winter compared to summer. But it is also found that for a given transport route, nighttime aerosol particles are more concentrated during summer compared to winter. Summer increase of emission intensity in the boundary layer, stronger exchange between the boundary layer and the free troposphere as well as enhanced altitude-related photochemical processes can lead to this observation. The nighttime samples are selected from our data set to calculate background aerosol characteristics for given air mass types at high altitude. Continental and regional air masses are not very different from each other, and from marine air masses for winter, but twice as more concentrated than marine air masses during summer.

On average, the marine Puy de Dôme aerosols distributions compare well with the distributions reported in the literature for clean marine air masses. However, they are more similar to the air masses classified by Van Dingenen et al. (2005) as free tropospheric than the ones classified as marine aerosols at the Monte Cimone station. The size distribution derived for continental air masses are considerably lower compared to those proposed by Whitby (1978) or Jaenicke (1993), but about five times higher during winter compared to the typical free tropospheric aerosol number distribution proposed by Jaenicke (1993). More recent measurements in the boundary layer background continental air masses compare better with our measurements (Tunved, 2003; Van Dingenen, 2005).

The seasonal variability in aerosol sources seems to be predominant over the continent compared to the seasonal variation of marine aerosol sources. We believe 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 chemistry-transport models.

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Table 1. Nighttime size distribution lognormal parameters for marine, continental and regional air masses for summer and winter conditions.

		Winter			Summer		
		σ	Dp_N (nm)	N (cm^{-3})	σ	Dp_N (nm)	N (cm^{-3})
Marine	Nucleation	1.5	20	17	1.4	20	5
	Aitken	1.6	36	260	1.6	32	545
	Accumulation	1.4	135	18	1.6	120	95
Continental	Nucleation	1.5	22	110	1.4	17	25
	Aitken	1.5	55	265	1.7	45	1000
	Accumulation	1.5	145	120	1.6	130	800
Regional	Nucleation	1.5	20	60	1.5	35	460
	Aitken	1.6	59	410	1.6	85	1025
	Accumulation	1.4	170	85	1.5	180	312

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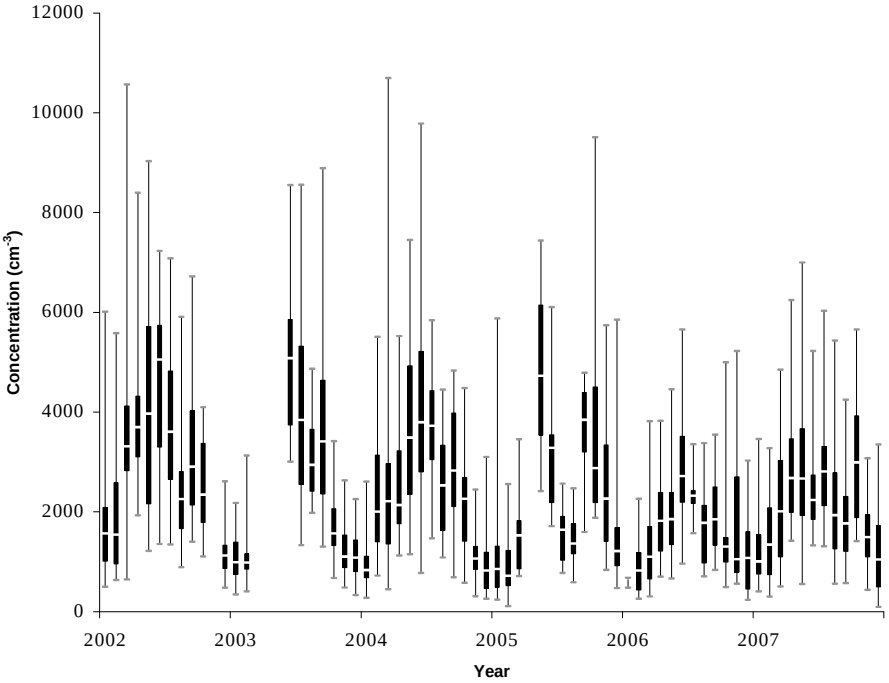

Fig. 1. Monthly median total number particle concentrations (Dp>10 nm), 25–75 percentile and minimum-maximum ranges over the 2002–2008 period.

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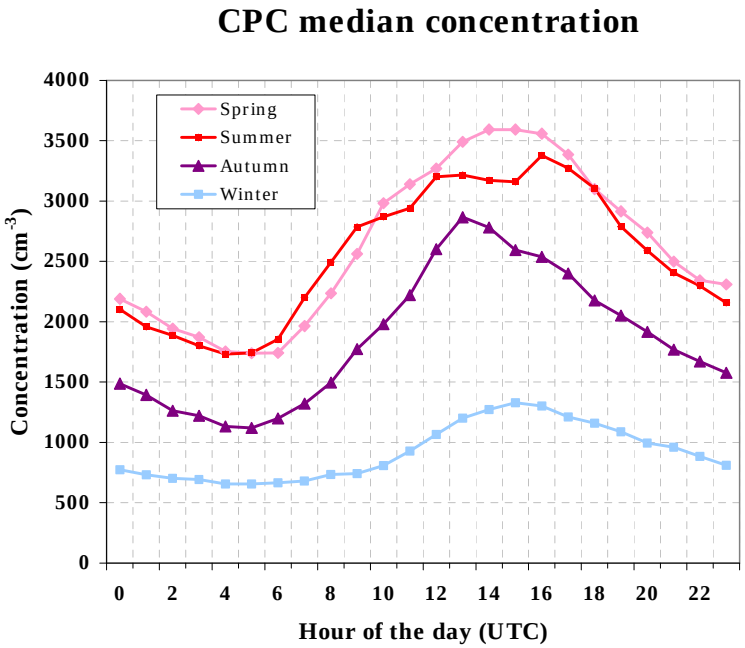

Fig. 2. Median diurnal variations (from 00:00 to 24:00 UTC) of total number concentrations obtained from CPC concentration calculated for each season over the 2002–2007 period.

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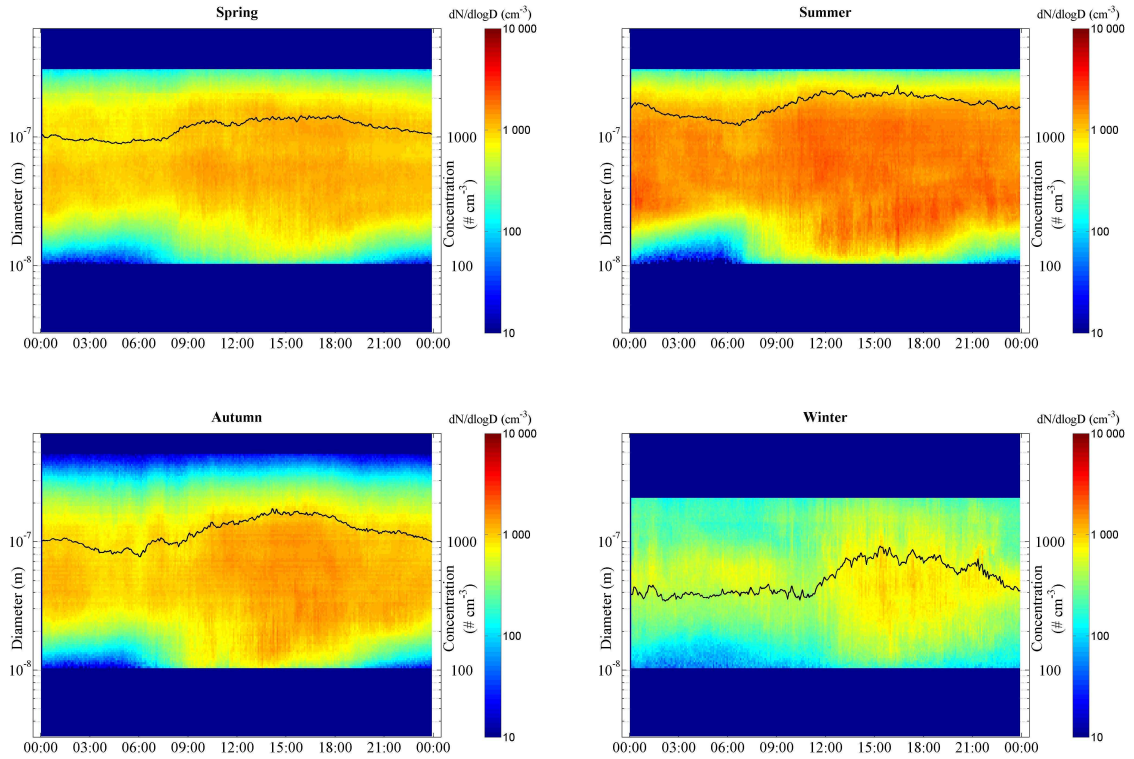

Fig. 3. Median diurnal variation of the aerosols number size distribution for each season calculated from SMPS measurements over the January–December 2006 period. X axis is the time from 00:00 UTC to 24:00 UTC, Y axis is the size of the aerosol (from 10 to 500 nm) and the normalized concentration (dN/dLogDp) is represented from the color bar. The total concentration is also shown as the black line (right axis).

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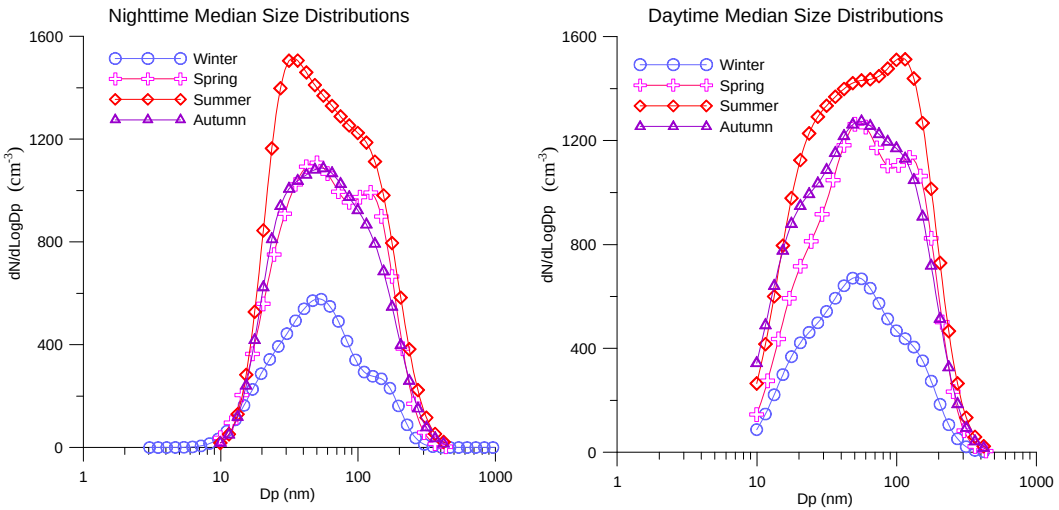

Fig. 4. Nighttime and daytime median size distribution for each season calculated over the January to December 2006 period, Nighttime: from 00:00 to 06:00 UTC; daytime: from 06:00 to 19:00 UTC.

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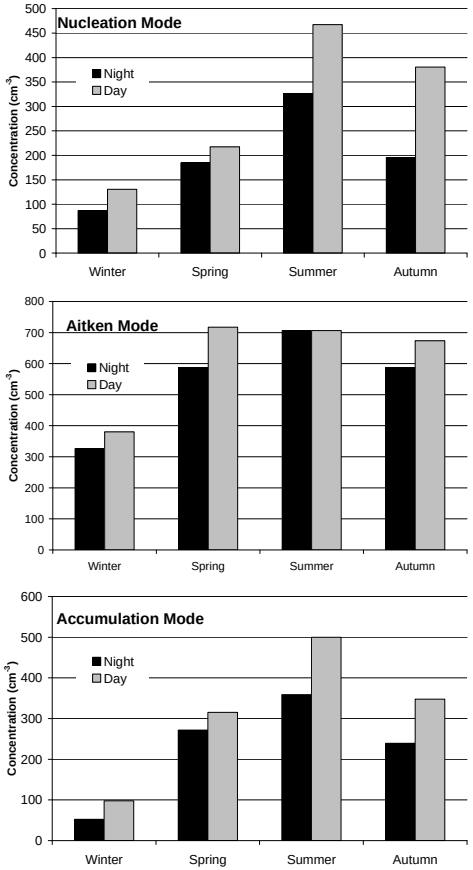

Fig. 5. Median number concentrations in the nucleation, Aitken, and accumulation mode for each season and for day (00:06 to 19:00 UTC) and night (06:00 to 19:00 UTC) periods obtained from the lognormal fitting procedure of the aerosol size distributions.

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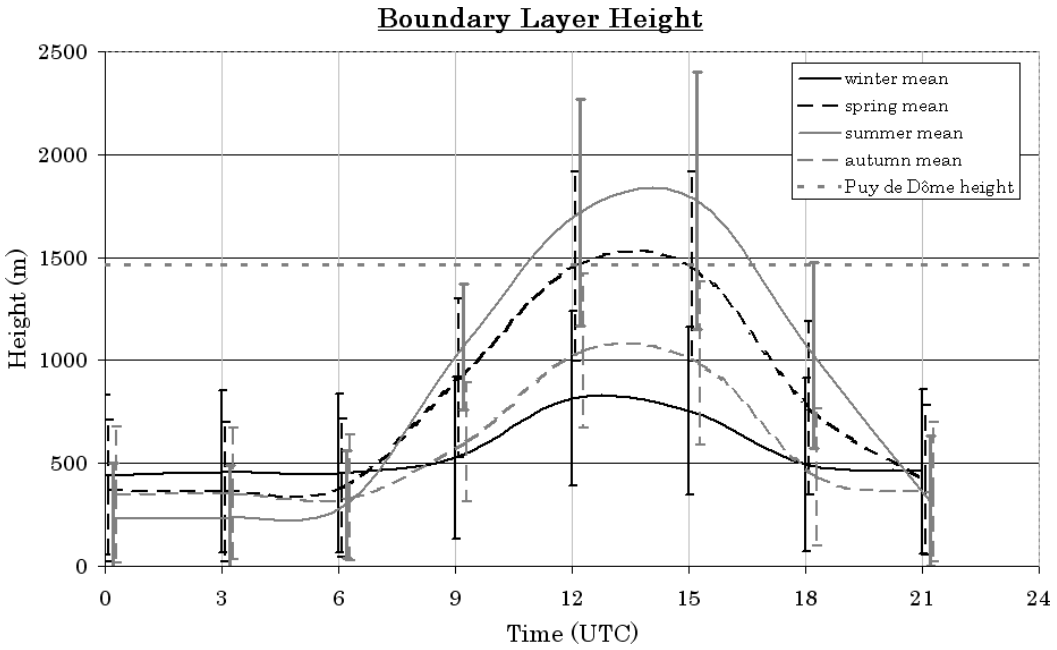

Fig. 6. Diurnal variation of the boundary layer height (computed with ECMWF, over the years 2003–2006) averaged for the four seasons, with the variability among each season pictured as the standard deviation.

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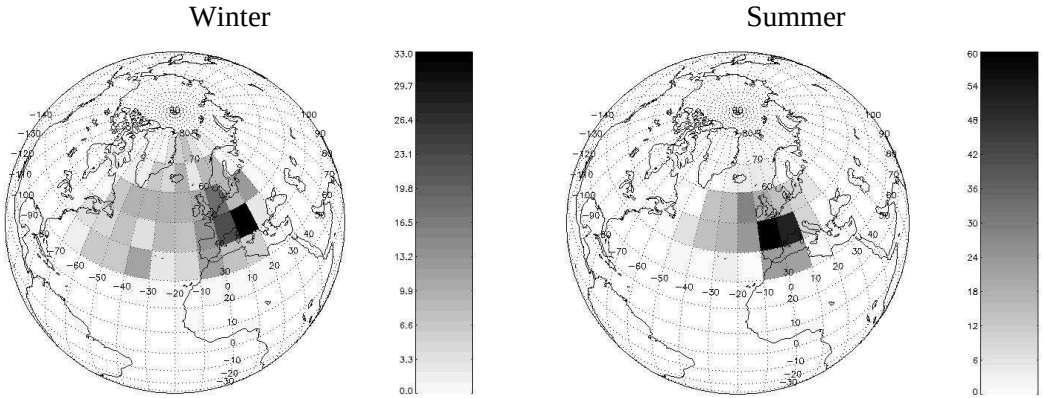

Fig. 7. Map of the number of three-days back trajectories endpoints calculated using the HYSPLIT transport and dispersion model over the 2003–2007 period on a day to day basis at 00:00 UTC.

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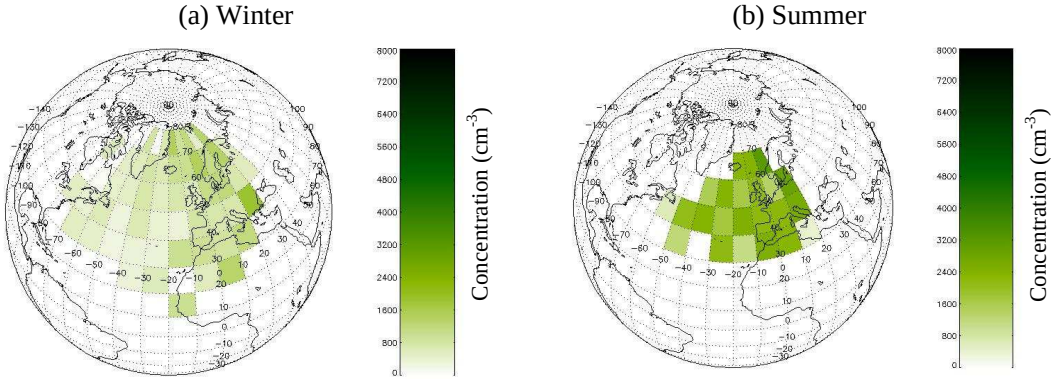

Fig. 8. Map of the median nighttime aerosol total number concentration (obtained from the CPC measurements) for each ensemble of back trajectories ending at the target zone.

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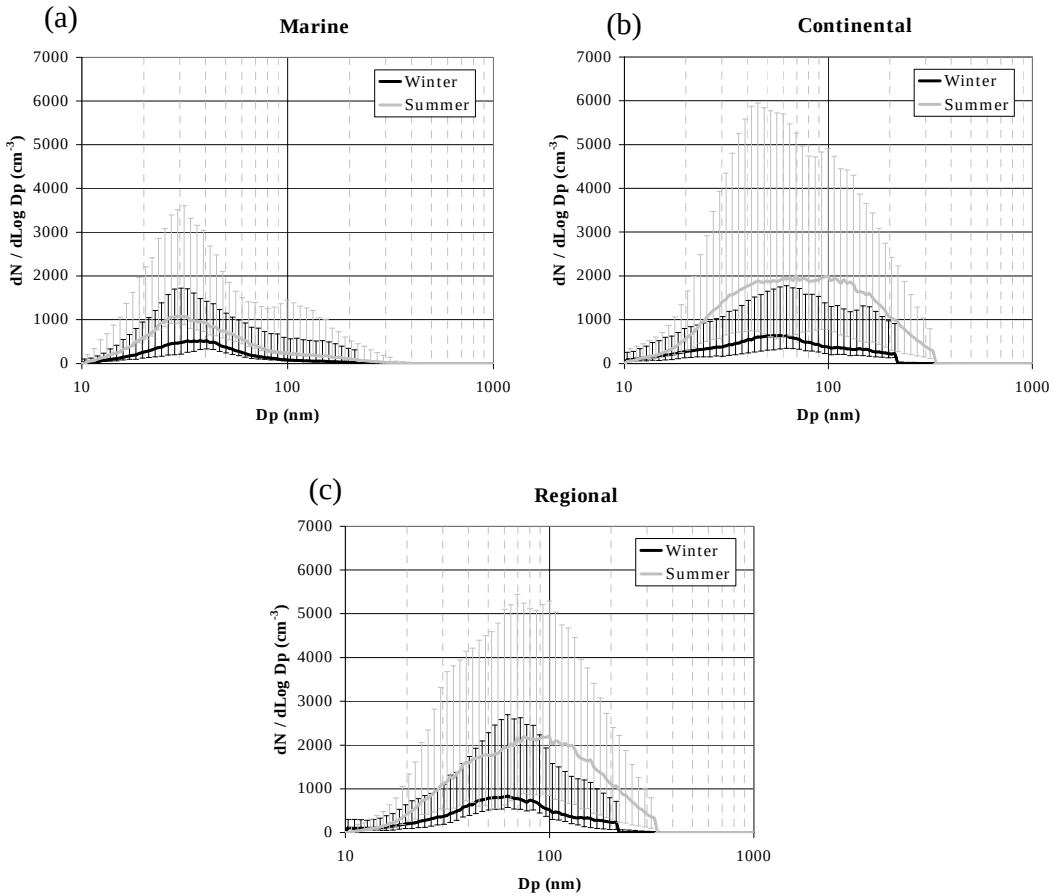

Fig. 9. Nighttime median size distribution and 25–75 percentile ranges for **(a)** marine, **(b)** continental and **(c)** regional air masses during winter and summer. See text for the definition of marine, continental and regional air masses.

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