

Submicrometer aerosol particle distributions in the upper troposphere over the mid-latitude North Atlantic—results from the third route of ‘CARIBIC’

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ABSTRACT

Particle number and mass concentrations of submicrometer aerosol particles were determined for the upper troposphere over the mid-latitude North Atlantic within the Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container project (CARIBIC, <http://www.caribic-atmospheric.com>). Between May 2001 and April 2002, 22 flights from Germany to the Caribbean were conducted using an automated measurement container on a B767 passenger aircraft. Spatial and seasonal probability distributions for ultrafine and Aitken mode particles as well as mass concentrations of particulate sulphur in 8–12 km altitude are presented. High particle number concentrations (mostly 2500–15 000 particles cm⁻³ STP) are particularly found in summer over the western North Atlantic Ocean close to the North American continent. The distributions together with an analysis of particle source processes show that deep vertical transport is the dominant process leading to most of the events with high particle number concentrations ($\gtrsim 8000$ particles cm⁻³ STP) for ultrafine particles as well as for Aitken mode particles. This study emphasizes the importance of deep vertical transport and cloud processing for the concentration of aerosol particles in the upper troposphere.

1. Introduction

The limited knowledge on aerosol particles in the Earth's atmosphere still causes one of the largest uncertainties concerning climate change (<http://www.ipcc.ch/SPM2feb07.pdf>). This deficiency lies with the complex chemical composition of aerosol particles, the great variety of chemical and physical processes they undergo, and their relatively short atmospheric residence time. In particular, the interaction between aerosol particles and clouds (indirect climate effects) is not well understood and incompletely represented in atmospheric models (Lohmann and Feichter, 2005). Investigations based on a cirrus cloud experiment conducted over Florida indicate that the aerosol in the free troposphere plays a much more important role in convective cloud development than previously thought (Fridlind et al.,

2004). This finding is confirmed by a modelling study (Yin et al., 2005), which also indicates that already cloud-processed particles from higher altitudes can be re-entrained into the cloud and thus influence cloud properties. Even the smallest particles, known as ultrafine particles (diameter $< \sim 10$ nm) might have an indirect influence on cloud properties. The reason is that new particle formation can produce high number concentrations of such ultrafine particles, exceeding background values by orders of magnitude. These particles grow by condensation to Aitken mode particles (~ 10 nm $<$ diameter $<$ ~ 100 nm) and can thus serve as cloud condensation nuclei (CCN) (Laaksonen et al., 2000; Pirjola et al., 2004; Kerminen et al., 2005). However, the importance of this process and more basically the relative contribution of individual particle sources or particle formation processes to the number concentration in the free troposphere are not well known.

In order to reduce the uncertainties associated with atmospheric aerosol particles, a combined approach of in situ experiments, remote sensing, and modelling studies is needed

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(Anderson et al., 2005; Andreae et al., 2005; <http://www.ipcc.ch/SPM2feb07.pdf>). As part of this approach, atmospheric measurements providing statistically relevant data with respect to space and time are necessary. Such data not only improve process understanding but also help to validate satellite retrieval algorithms and can be used to verify model results at an increased level of sophistication.

From 1997 to 2002, aerosol particle and trace gas concentrations were measured in 8–12 km altitude in the upper troposphere (UT) and lower stratosphere (LS) within the Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container project (CARIBIC, Brenninkmeijer et al., 1999, <http://www.caribic-atmospheric.com>). Using a passenger aircraft (Boeing 767-300ER of LTU International Airways, Düsseldorf), the number concentration and the elemental composition of aerosol particles in the UT/LS were investigated. During 77 flights and more than 570 000 flight kilometres (~ 14.5 times around the globe) from Germany to the Indian subcontinent (49 flights), to Southern Africa (6) and to the Caribbean (22), aerosol particle data were collected, yielding a unique data set. Having discussed aerosol data on the Indian route (Martinsson et al., 2001; Heintzenberg et al., 2002; Papaspiropoulos et al., 2002; Hermann et al., 2003) and on the Africa route (Heintzenberg et al., 2003), we present here the UT particle concentration measurements from the third CARIBIC route, namely to the Caribbean. Inferred spatial and seasonal distributions of submicrometer particles yield probability densities which are representative for the upper troposphere over the mid-latitude North Atlantic Ocean.

2. Experimental

In this section only a concise description of the CARIBIC system and the respective aerosol measurements will be presented. For more information about CARIBIC we refer the reader to Brenninkmeijer et al. (1999), Brenninkmeijer et al. (2007) and <http://www.caribic-atmospheric.com>. The aerosol measurement techniques are described in Hermann and Wiedensohler (2001), Papaspiropoulos et al. (2002), Hermann et al. (2003) and references therein.

In the CARIBIC project, aerosol and trace gas instruments are installed in a modified airfreight container, being a compact automated observatory. This container was flown in the forward cargo compartment of the B767-300ER on a monthly basis. An aerosol and trace gas inlet system permanently mounted on the bottom side of the aircraft fuselage ten metres from its nose provided ambient air to the instruments in the cargo compartment. After completing an outbound and an immediate return flight the container was unloaded and the collected data and samples were analysed. The 22 CARIBIC flights to the Caribbean were conducted from May 2001 to April 2002. The respective flight tracks are displayed in Fig. 1. They cover most of the North Atlantic Ocean at mid-latitudes.

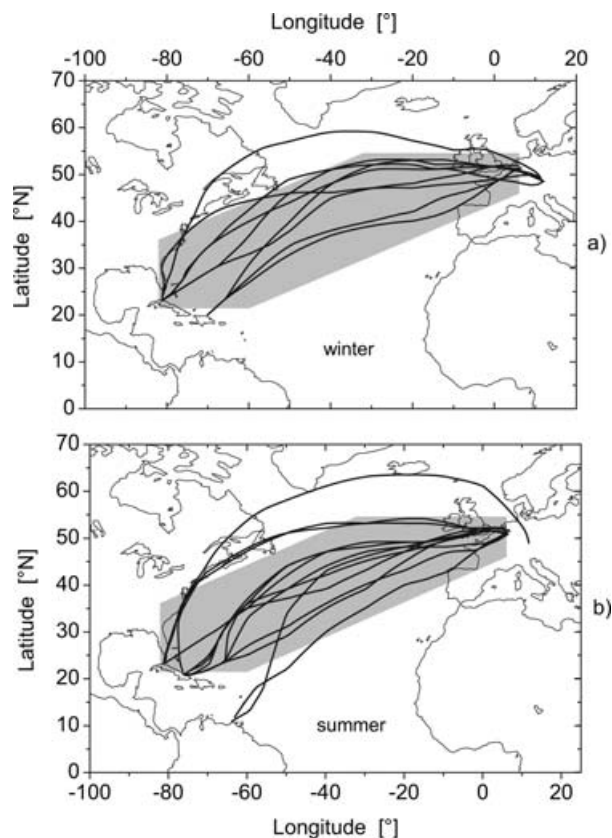


Fig. 1. CARIBIC flight tracks along the Caribbean route for (a) winter and (b) summer. The grey shaded polygon indicates the area which covers 93% of all measurements in the UT.

The CARIBIC measurement container for the LTU B767 housed two aerosol units comprising three condensation particle counters (CPCs) and one particle sampler. The CPCs (modified TSI models 7610) measured integral particle number concentrations in three size ranges with 2 s time resolution. The lower threshold diameters effective at cruise altitude were ~ 4 , ~ 12 and ~ 18 nm, respectively (Hermann and Wiedensohler, 2001). The upper threshold diameter of $1.3 \mu\text{m}$ was determined by the 50% transmission efficiency of the inlet system (Hermann et al., 2001). Raw data were corrected for particle losses in the inlet and in the sampling line, for pressure-dependent CPC flow rates, for CPC counting efficiencies and for coincidence in the CPC optics (*cf.* Hermann et al., 2003). All concentrations presented in this work were converted to standard conditions (STP: 1013.25 hPa and 273.15 K). The difference of the readings of the first two CPCs yields the number concentration of ultrafine particles (here defined as particles with diameters between 4 and 12 nm, N_{4-12}), which can be regarded as an indicator for new particle formation events.

Concentrations measured by the second CPC (N_{12}) strictly speaking represent the sum of Aitken mode (~ 10 nm < diameter < ~ 100 nm) and accumulation mode (~ 100 nm <

diameter $< \sim 1000$ nm) particles. However, in the UT the Aitken mode number concentration normally dominates strongly over the accumulation mode number concentration (e.g. Clarke and Kapustin, 2002; Heintzenberg et al., 2002) and hence N_{12} can be considered as the number concentration of Aitken mode particles only. In this study, no data from the third CPC (N_{18}) will be presented, because the resulting distributions match the N_{12} distributions well, however, with on average $\sim 15\%$ lower concentrations. Experimental uncertainties in N_{12} and N_{4-12} amount to ± 10 and $\pm 35\%$, respectively (cf. Hermann et al., 2003).

The CARIBIC particle sampling system consisted of 14 parallel impactors, which collected particles in the size range from 65 nm to 1.3 μm (Papaspiropoulos et al., 1999). Samples were taken sequentially (2.5 h duration) and one for each whole flight (~ 8 h). After each flight, samples were analysed for elemental composition using particle induced X-ray emission (PIXE) at Lund University.

Besides the aerosol instrumentation, the CARIBIC container also housed trace gas measurement devices for CO (Brenninkmeijer et al., 1999), O_3 (Zahn et al., 2002), NO/NO_y (Ziereis et al., 2000) and an air sampler (Brenninkmeijer et al., 1999). Furthermore, aircraft flight parameters, for example, pressure altitude, aircraft position and true air speed, were recorded via one of the four aircraft communication buses (ARINC). To facilitate data interpretation, backward trajectories as well as horizontal maps and vertical cross-sections of meteorological parameters (e.g. potential vorticity) along the individual flight tracks were calculated by KNMI (Scheele et al., 1996; http://www.knmi.nl/samenw/campaign_support/CARIBIC/).

3. Data analysis

In this study, only particle concentrations measured at cruise altitude between 28 000' and 37 000' (8.5–11.3 km) were analysed whereas aircraft ascents and descents were omitted (cf. Hermann et al., 2003). Moreover, about 82% of these measurements were conducted on flight levels between 31 000' and 35 000' (9.4–10.7 km) altitude, that is, in a quite narrow altitude range. Within the chosen altitude range, differences in particle number concentrations are mainly determined by the actual meteorological situation and particularly in the LS by the distance to the tropopause and not by the absolute altitude. Hence data were not classified with respect to altitude. To distinguish between tropospheric and stratospheric dominated air masses, the in situ measured ozone values and the chemical tropopause definition given by Zahn and Brenninkmeijer (2003) were used. They found that the ozone tropopause threshold value at mid-latitudes undergoes a uniform seasonal cycle that can be well approximated by a sinusoidal function, which minimizes in October/November at 71 ppb and maximizes in April/May at 123 ppb. Accordingly, measurements with ozone mixing ratios either above or below this threshold value are attributed to either the LS or the UT, respectively. As the particle samples were taken over

a much longer period (2.5 h), for the classification of UT and LS samples a different method based on the potential vorticity (PV) was used (cf. Martinsson et al., 2005). The respective threshold value was chosen as 2 PVU.

For the data analysis, the 22 flights were divided into a 'summer' half-year from May to August 2001 and a 'winter' half-year from November 2001 to April 2002. This division is a compromise between the desire for information about seasonal differences in the particle distributions and the need for a sufficient number of flights in each subset in order to yield sound statistics.

In comparison to the flight tracks on the Indian route, the flight tracks on the Caribbean route cover a much larger area, and spatial distances between individual flights at a given longitude can be tens of degree latitude. However, by restricting the analysis to the latitude band 21.5°N to 54.5°N this spread is substantially reduced. Moreover, 93% of all particle concentrations measured in the UT fall into a much smaller corridor which is indicated as grey shaded area in Fig. 1. Hence, the following results can be regarded as representative for that specific area, that is, the mid-latitude North-Atlantic Ocean.

Spatial probability distributions of ultrafine particles and Aitken plus accumulation mode particles in the UT were calculated in the same way as described in Hermann et al. (2003). Each seasonal and particle size range subset of concentrations was grouped into 8° longitude bands between -8°W and 6°E . Within each band, the data were distributed into 30 concentration bins of equal logarithmic width ($\Delta \ln N = 0.065$ and 0.103 for N_{12} and N_{4-12} , respectively). Each bin contains more than 6500 data points from at least five flights. The resulting distributions give the probability density function for the particle number concentration at a given longitude, in the altitude range 8.5–11.3 km over the mid-latitude North Atlantic Ocean.

4. Results and discussion

The probability distribution for N_{12} in the UT over the mid-latitude North Atlantic Ocean is shown in Fig. 2. In this graph, colours give the percentage of all data points in a particular longitude band that fall into a certain concentration bin. To facilitate comparison with the distributions on the Indian route (Hermann et al., 2003), the same y-axis scale and the same colour code was chosen.

In summer (Fig. 2a), Aitken mode particle concentrations over Western Europe (east of -12° longitude) mostly range from 1200 to 6000 particles cm^{-3} STP. The respective distribution is quite similar to the one observed over southeastern Europe on the Indian route (cf. Hermann et al., 2003, Fig. 5a). Likewise, previous measurements over the British Isles by de Reus et al. (1998) yielded mean concentration values in about the same range (800–6400 particles cm^{-3} STP).

More westward, over the central North Atlantic Ocean between about -20° and -40° longitude, the N_{12} range is quite similar to the one over Western Europe (Fig. 2a). The relatively low

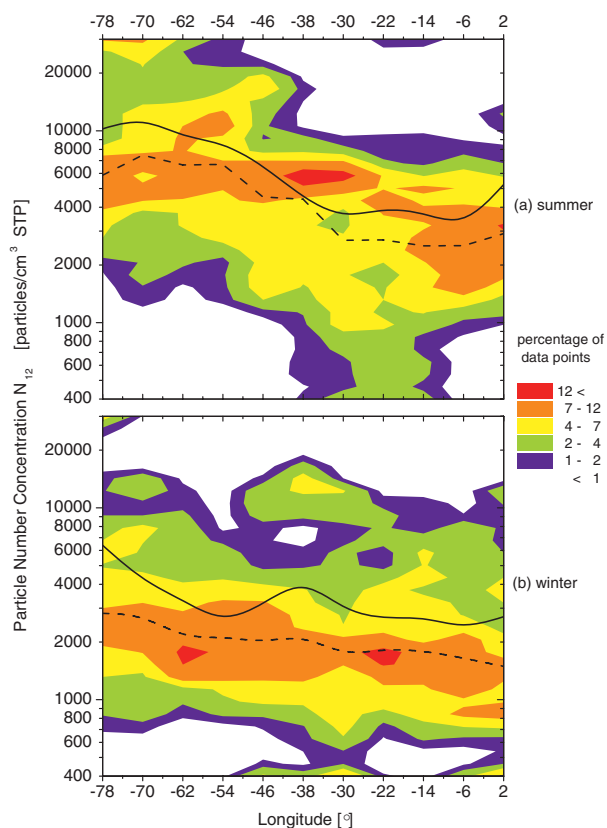


Fig. 2. Probability distribution of Aitken plus accumulation mode particles (N_{12}) in the UT in (a) summer and (b) winter along the Caribbean route. Colours indicate the percentage of all particle measurements in a longitude band that fall into a particular concentration bin. The solid line represents the mean value for each longitude band, the dashed line the respective median.

concentrations in the three longitude bins ‘ -14° ’, ‘ -22° ’ and ‘ -30° ’ originate almost exclusively from measurements conducted during one flight in May 2001 (out of ten in total for each bin) and hence might represent a statistical bias. West of approximately -42° longitude, over the Sargasso Sea and close to the North American continent, N_{12} becomes highly variable and reaches high values up to 30 000 particles cm^{-3} STP. Mostly, between 2500 and 15 000 particles cm^{-3} STP were observed. The high number concentrations and the large variability may be caused by frequent strong convective activity over the central and southeastern United States (Li et al., 2005), transporting particles and particle precursor gases upward into the UT (Thornton et al., 1997; Talbot et al., 1998; Brunner et al., 2001). Detailed modelling studies of deep convective clouds confirm this particle transport way and the occurrence of particle formation in the outflow regions (Zhang et al., 1998; Yin et al., 2005; Ekman et al., 2006). Respective number concentrations for the UT lie in the same range as observed by CARIBIC. Another source of UT/LS particles are aircraft emissions, which have their maximum over

North America in the region between $\sim 34^\circ$ and $\sim 43^\circ$ northern latitude and $\sim 95^\circ$ and $\sim 77^\circ$ western longitude (Garber et al., 2005). Particles emitted in that area are likely to be transported by the prevailing westerlies into the region probed by CARIBIC. Besides convection, the other effective vertical transport mechanism at mid-latitudes are warm conveyor belts (WCBs), associated with cyclones (Stohl, 2001). Over North America, cyclones mainly form in the lee of the Rocky Mountains and transport air masses from the lower troposphere via WCBs into the UT (Li et al., 2005). Furthermore, the West Atlantic storm track is a region where cyclogenesis takes place. In summer, one of the primary areas where WCB transport pathways reach the UT lies in the Atlantic storm track region between $\sim 30^\circ$ and $\sim 50^\circ$ northern latitude and $\sim 20^\circ$ and $\sim 40^\circ$ western longitude (cf. Stohl, 2001, Fig. 1). However, comparing the relative contribution to vertical transport that reaches the UT at northern mid-latitudes over the North Atlantic, deep convection seems to clearly dominate over WCBs in summer, as shown by a model comparisons made by Hess (2005) (cf. Fig. 9, the isentropic surface of that figure corresponds to flight levels along the Caribbean route within ± 15 K). In this publication, also the strong convective activity in summer over the Caribbean Sea and the Gulf of Mexico becomes clearly visible. As CARIBIC backward trajectories indicate, part of the probed air masses close to the American continent is coming from this region. Hence there is a tropical influence on the high number concentrations in the three most westerly longitude bins of Fig. 2a (i.e. ‘ -78° ’, ‘ -70° ’ and ‘ -62° ’).

Aitken mode particle number concentrations over the mid-latitude North Atlantic Ocean in winter are generally lower compared to summer (Fig. 2b). Over Western Europe and the central North Atlantic Ocean, N_{12} mostly ranges from 700 to 5000 particles cm^{-3} STP and increases only little over the western North Atlantic (1000–6000 particles cm^{-3} STP). This range of observation is in good agreement with the measurements made during the SONEX (Subsonic assessment Ozone and nitrogen Oxides Experiment) campaign in the North Atlantic flight corridor (NAFC) (cf. Thompson et al., 1999). Number concentrations obtained by Clarke and Kapustin (2002) for the UT over the Pacific lie in the same range. According to Eckhardt et al. (2004), the two regions should be comparable with respect to vertical transport by WCBs. Concerning deep convection, however, there are differences for northern hemispheric summer (Hess, 2005). The contribution to particle concentrations by aircraft emissions will likely be lower over the Pacific, since the North Atlantic is one of the regions with the highest aircraft density in the world.

One plausible reason for the lower N_{12} values in winter can be the reduced convective activity over North America (Brunner et al., 2001; Hess, 2005). Likewise, the contribution to vertical transport by WCBs into the region probed by CARIBIC seems to be lower in winter compared to summer (cf. Stohl, 2001, Fig. 1). According to a 15-yr WCB climatology by Eckhardt et al. (2004), the mass flux into the UT over the North Atlantic caused by WCBs in winter is much higher than in summer, but it seems

that the majority of WCB pathways actually do not reach the cruising altitudes of airliners (*cf.* Hess, 2005, Fig. 9; Eckhardt et al., 2004, Fig. 5). As the number of aircraft flights over the northeastern USA in winter is reduced by only a few percent compared to summer (Garber et al., 2005), but the particle probability distributions shows much lower concentrations, this is a first indication that aircraft emissions are not the dominant sources for N_{12} particles over the western North Atlantic Ocean (*cf.* discussion of Fig. 5).

In recent years several global atmospheric models have been developed and tested which included specific aerosol microphysics modules (e.g. Adams and Seinfeld, 2002; Liu et al., 2005; Spracklen et al., 2005; Lauer and Hendricks, 2006; Verma et al., 2007). Unfortunately, presented data and comparisons with experimental data focused on surface concentrations or zonal averaged vertical cross-sections and to our knowledge, there are no regional or global concentration maps available for the UT. However, it would be highly desirable to compare CARIBIC data with such models in order to support data interpretation and to evaluate model performance (Lucas and Akimoto, 2006).

The distribution of the ultrafine particle number concentration is displayed in Fig. 3. In summer (Fig. 3a), N_{4-12} values over Western Europe lie in the range of less than 50–

1000 particles cm^{-3} STP, indicating only moderate particle formation activity. In one fifth of all cases there are nearly no ultrafine particles at all. It should be noted that N_{4-12} values of ~ 50 particles cm^{-3} STP or less might arise from statistical fluctuations in the particle concentrations measured independently by the two CPCs. Hence these low concentrations indicate effectively the likely absence of ultrafine particles and absolute numbers are uncertain. The range of concentrations displayed in Fig. 3a is again in good agreement with results presented by de Reus et al. (1998) for the same region and time of the year. However, the values are quite different to the ones obtained for southeastern Europe, where particle formation was observed quite regularly giving mostly 200–3500 particles cm^{-3} STP (*cf.* Hermann et al., 2003, Fig. 7a). As the two regions are located at approximately the same latitude band, with the latter being shifted by approximately 20° towards the east, this might be indicative of the influence of the European continent (precursor sources and deep convection) on the particle formation activity in the UT.

Over the central North Atlantic ultrafine particles occur less frequently, but if so, then in approximately the same concentration range as over Western Europe. In 35% of all cases N_{4-12} values are close to zero. This picture changes west of approximately -64° longitude, where over the Sargasso Sea ultrafine particles are observed quite regularly with concentrations of mostly 200 to 14 000 particles cm^{-3} STP, indicating particle formation activity in the UT. Again, aircraft emissions (e.g. Brock et al., 2000) and vertical transport, for example, by deep convective clouds (Liu et al., 2001; Twohy et al., 2002; Bertram et al., 2007) are the most likely sources.

A noteworthy aspect is that the ultrafine particle concentrations presented here might not only be influenced by the geographical location (i.e. longitude and latitude), but also be affected by the measurement time, that is, the local time of day (LTD). Because of airline operating conditions, the CARIBIC aircraft probed specific regions of the Caribbean route always at about the same time of day. The measurements over the western North Atlantic were carried out mostly during local daytime (11–20 LTD), whereas the measurements over the eastern North Atlantic took place late at night and in the morning hours (03–12 LTD). These time windows hold for both, summer and winter flights. Hence, the distributions of ultrafine particles shown here should also reflect any diurnal variation of particle source processes, for example, particle formation in the context of deep convective clouds, which includes photochemistry. Aitken mode particles, which have a longer lifetime, are less sensitive to this effect.

The N_{4-12} particle distribution for winter is less coherent compared to summer (Fig. 3b). Ultrafine particle concentrations found over Western Europe can be higher, lying mostly either below 50 particles cm^{-3} STP or between 150 and 2000 particles cm^{-3} STP. Again, approximately 20% of all measurements show nearly no ultrafine particles. Over the central North

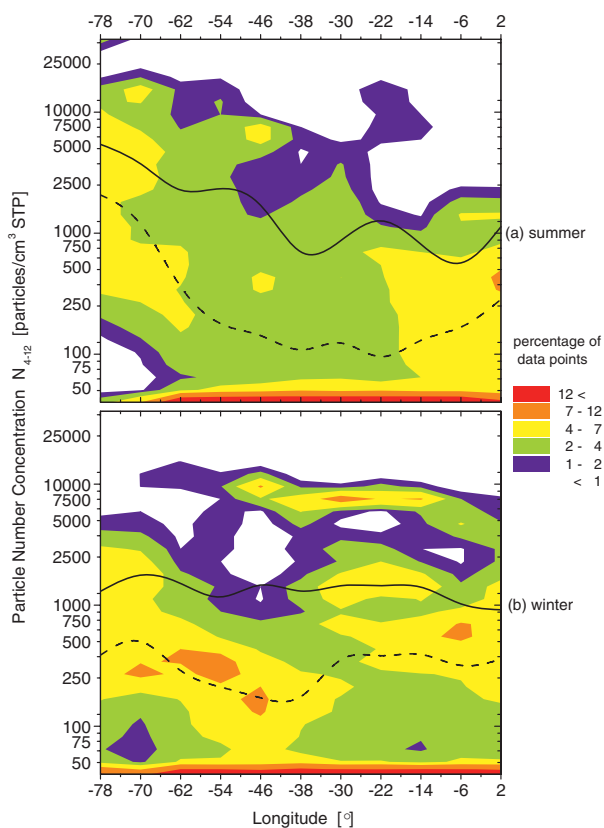


Fig. 3. Probability distribution of ultrafine particles (N_{4-12}) in the UT in (a) summer and (b) winter along the Caribbean route.

Atlantic, N_{4-12} particles were observed more frequently and with higher variability compared to summer. N_{4-12} values close to the North American continent are lower and mostly lie either below 50 particles cm^{-3} STP or range from 150 to 3000 particles cm^{-3} STP. For both seasons, ultrafine particle concentrations observed on the Caribbean route lie in the same range as reported by Clarke and Kapustin (2002) for the eastern Pacific Ocean.

The higher ultrafine particle concentrations over the eastern North Atlantic and Western Europe in winter might be explained by the stronger deep convective activity over the ocean compared to summer (*cf.* International Satellite Cloud Climatology Project (ISCCP), <http://isccp.giss.nasa.gov/>). Conversely, the vertical transport by deep convection is reduced in winter over the continents. Hence, the N_{4-12} values close to North America are lower.

The elemental analysis of particles sampled in the UT over the mid-latitude North Atlantic Ocean yielded that sulphur was the most abundant element and had the highest concentrations, in agreement with former studies (e.g. Papaspiropoulos et al., 2002; Kojima et al., 2004). Interpreting this result, it should be considered that the PIXE analysis method generally cannot detect light elements, like for instance carbon and hence organic material, because of technical reasons. In the near future, however, proton elastic scattering analysis (PESA) will extend the analytic capability on aerosol particles within CARIBIC (*cf.* Nguyen H. N. and B. G. Martinsson, Analysis of C, N and O in Aerosol Collected on an Organic Backing using Internal Blank Measurements and Variable Beam Size, Nuclear Instruments and Methods B, in press).

The spatial distribution of particulate sulphur along the Caribbean route is shown in Fig. 4. Displayed are individual samples (circles) and median values (bars) in four longitude bands. These bands were chosen by the criterion of approximately equal number of flights per band. In general, the features in the particulate sulphur concentration are not as pronounced as in the particle number concentration. For summer, sulphur concentrations mostly range from 4 to 28 ng m^{-3} STP. However, during one flight in August, 2001 for two successive samples two of the highest concentrations ever measured during CARIBIC were recorded with 66 and 96 ng m^{-3} STP (grey circles). These high concentrations are common in the upper part of the lowermost stratosphere (Martinsson et al., 2005). However, PV values for the respective sampling periods remain below 1.7 PVU, with 85% below 1.5 PVU, and hence are too low to indicate air masses from that part of the lowermost stratosphere. In the upper troposphere such high particulate sulphur concentrations are scarce indeed. Out of 155 tropospheric samples taken during the CARIBIC-LTU period only seven observations of particulate sulphur concentrations in excess of 40 ng m^{-3} STP were made. Five-day backward trajectories show no, and 14-d backward trajectories only little evidence for the possible uptake of polluted air over continents. Likewise, trace gas analysis of the respective air samples (altogether seven) does not

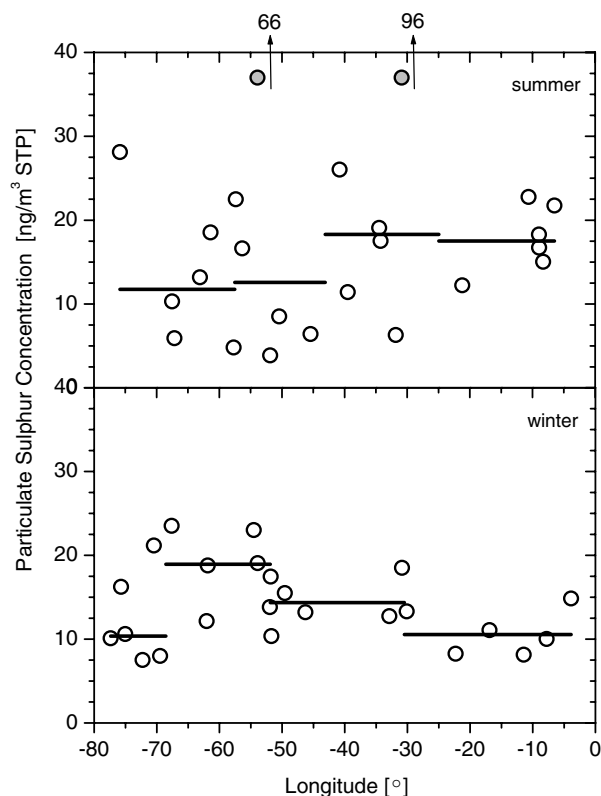


Fig. 4. Particulate sulphur concentrations (ng m^{-3} STP) along the Caribbean flight route. Displayed are the individual samples (circles) and the median concentrations (bars) for four longitude bands. Band limits were determined by the criterion of approximately equal number of measurements per longitude band. The two samples indicated by the grey circles lie outside the indicated y-axis range.

show any unusually elevated values. The concurrently measured greenhouse gases, namely CO_2 , CH_4 , N_2O , SF_6 and also halocarbons and hydrocarbons do not give a clue for pollution. N_2O concentrations for all seven air samples are larger than 314 pbb, which indicates tropospheric air masses. What does however correlate are O_3 and ^{14}C . With ^{14}C being elevated in the stratosphere, this cosmogenic isotope is a sensitive indicator for stratospheric air. Moreover, using the chemical tropopause definition (*cf.* Section 3), about 16 and 39% of the sampling time of the 66 and 96 ng m^{-3} STP sample, respectively, is indicated as 'stratospheric'. The PV map and cross-section show that the aircraft flew just below the tropopause parallel to the northern edge of a decaying PV-streamer that extended from Europe in a southwestward direction over the Atlantic (http://www.knmi.nl/samenw/campaign_support/CARIBIC/110801/index.html). In this way the aircraft took advantage of a region with low and locally even westward directed winds. The wind shears on the edge of PV streamers are preferred regions for mixing of stratosphere and troposphere air by dynamically generated turbulence. Hence we conclude that the

two high particulate sulphur concentration samples measured on the August 2001 flight represent a several weeks old aerosol (no indication for recent pollution) with some influence of stratospheric air.

In winter, the range of observed particulate sulphur concentrations is slightly smaller compared to summer (Fig. 4). Respective concentrations lie between 8 and 24 ng m⁻³ STP and regional mean values fall into in the same range as in summer (10–19 ng m⁻³ STP). The difference is, however, that there is a spatial shift, from low values over the western North Atlantic Ocean in summer to low values over Western Europe in winter. This feature is consistent with the picture for the particle number concentration given above, because deep convection reduces particle mass by activation and removal of larger particles.

One of the main, still open questions concerning the UT/LS aerosol, pertains to the relative contributions of different particle sources to the aerosol load in the UT/LS. To get an estimate of that, we used several tracers to identify source processes or regions of aerosol particle number concentration. Air originating from the lowermost stratosphere mostly contains an aged aerosol (Hamill et al., 1997) and can be identified using the in situ measured ozone concentrations (*cf.* Section 3). Particle number concentrations are rather low (<a few hundred particles cm⁻³ STP) and the concentration time series is rather even. In contrast, air influenced by surface sources can be identified by elevated CO mixing ratios and by using backward trajectories. This vertical transport is usually associated with clouds, which can be seen in the respective satellite pictures (*cf.* http://www.knmi.nl/samenw/campaign_support/CARIBIC/). Particle number concentration peaks caused by vertical transport are rather broad (several minutes in time series, corresponding to a few tens of kilometres in flight distance) and are highly structured compared to the background (*cf.* Wang et al., 2000). Part of this variability is caused by lightning events in deep convective clouds, which can

produce high particle number concentrations (Huntrieser et al., 2002). For this study, we used all three sources of information: backward trajectories, particle number peak form and an increase of the mean CO concentration by at least 10 ppb during the peak period compared to the CO values before and after the peak, to identify air masses which were brought into the UT/LS by relative fast vertical transport.

To estimate the contribution of aircraft emissions to the UT/LS aerosol, we used the in situ measured NO and NO_y mixing ratios as described in Schlager et al. (1997) or Anderson et al. (1999). Unfortunately, these data were only available for three flights in March 2002, because the NO_y instrument was incorporated in the CARIBIC payload only after spring 2002. Therefore, the following analysis is restricted to these three flights and the obtained results are representative only for that time of the year. Particle number concentration peaks caused by aircraft emissions are short spikes (few seconds to minutes in time series). As an aircraft plume ages, its signature wanes, first in H₂O and CO₂, subsequently in NO₃, and in particle concentrations. Hence, only fresh aircraft emissions with high particle concentrations can be identified directly and an estimate of the contribution to the background aerosol is not made here. For the source analysis, we used the particle number peak form and the occurrence of a similar peak in NO and in the NO/NO₃ ratio (>0.2 over surrounding value) as criteria in order to identify the contribution of aircraft to the UT/LS particle number concentration.

In Fig. 5, a histogram of all N₁₂ values measured during the three March 2002 flights is given (UT plus LS). This frequency distribution was calculated using 13 logarithmic equally spaced concentrations bins between 500 and 40 000 particles cm⁻³ STP. The distribution is roughly lognormal tailed towards higher concentrations and has its maximum slightly below 2000 particles cm⁻³ STP in agreement with previous data presented by Thompson et al. (1999). This consistency gives some

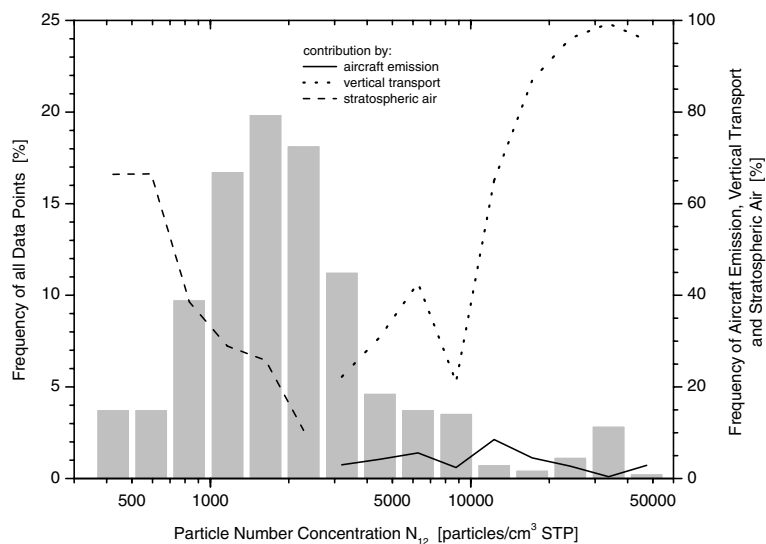


Fig. 5. Histogram of N₁₂ particle number concentrations for the three CARIBIC flights in March, 2002. Shown are the probabilities for all data points (UT plus LS) as grey bars and the relative contribution to the individual bars by aircraft emission (solid line), vertical transport (dotted line) and stratospheric air masses (dashed line). Bars are displayed at the logarithmic median of the bin concentration range. The first and the last bin represent all values smaller than 500 particles cm⁻³ STP and larger than 40 000 particles cm⁻³ STP, respectively.

confidence that although based on three flights only, the presented results are not biased by individual meteorological conditions.

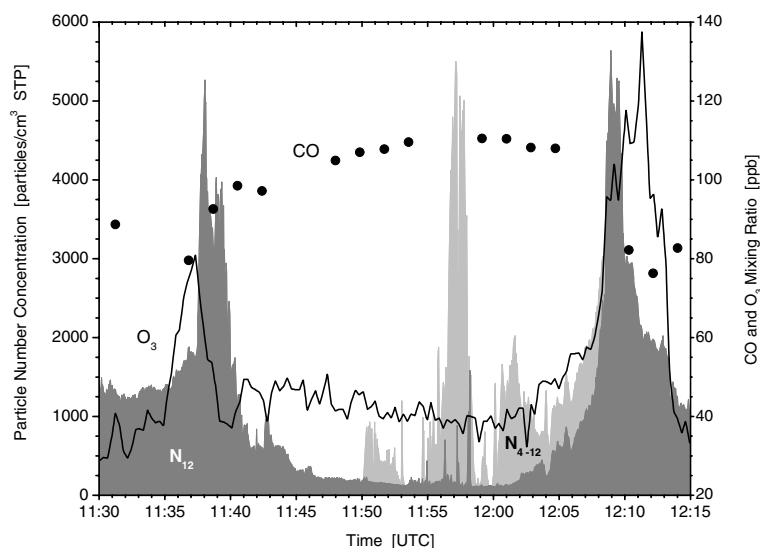
As Fig. 5 shows, N_{12} values over the North Atlantic, which are larger than $10\,000$ particles cm^{-3} STP coincide with and are probably caused by vertical transport processes (dotted line). In contrast, aircraft emissions contribute only $\sim 4\%$ on average to these particle concentrations (solid line). As particles produced by aircraft emissions or lightning were hard to distinguish with the available trace gas information, we decided to attribute all small spikes in regions we found influenced by vertical transport to lightning/vertical transport. Consequently the relative contribution of aircraft emissions to high aerosol particle concentrations is underestimated. Approximately one-fifth of all probed air masses showed influence of vertical transport. Assuming a regular distribution of aircraft emissions within the NAFC, its relative contribution should be higher by approximately 25%. Even including this correction, the relative contribution of aircraft emissions to high particle concentrations in the UT/LS in March is small, only about 5%. This value is in good agreement with the one found by Wang et al. (2000), who estimated a 6–7% contribution by aircraft to high particle number concentrations of particles larger than 8 nm over the mid-latitude North Atlantic for October/November 1997.

Figure 5 also shows that the sum of vertical transport and aircraft emission processes on average accounts for more than 92% of all N_{12} values larger than $10\,000$ particles cm^{-3} STP. This finding implies that other particle source processes, like particle formation due to mixing of tropospheric and stratospheric air masses (de Reus et al., 1998; Zahn et al., 2000; Khosrawi and Konopka, 2003) or particles generated by atmospheric waves (Nilsson et al., 2000), contribute only little to such strong events. It should be noted, however, that below $10\,000$ particles cm^{-3}

STP the relative contribution of both aircraft emissions and vertical transport decreases and other processes might become important. However, as lower concentrations likely represent older air masses, which already experienced some degree of mixing with background air, the decrease of both curves can also be explained by the loss of the source signature of the respective peaks. Therefore, particle concentrations in the middle of the concentration range cannot clearly be attributed to any one of the sources.

At the lower end of the particle concentrations shown in Fig. 5, below 700 particles cm^{-3} STP, approximately two third of all concentrations were measured in air masses, which show a stratospheric signature. This result is in agreement with the global mean vertical circulation pattern, which includes a mean downward transport of aged air masses from the stratosphere into the troposphere at mid- to high-latitudes. However, there are also cases, where tropospheric air masses show very low particle number concentrations. One such case where an air mass originating from the lowermost part of the troposphere shows very low N_{12} values is presented in Fig. 6. During the flight from Düsseldorf to Puerto Plata on March 7, 2002, elevated CO mixing ratios of ~ 108 ppb and low ozone values of ~ 45 ppb were observed over 20 min between -27.5° and -30.4° longitude and 39.4° and 39.0° latitude. Both trace gases indicate a fast vertical transport of boundary layer air masses. The respective trajectories and satellite pictures show that a high-pressure system west of Portugal transported low level air from Europe southwestward to the Atlantic Ocean (*cf.* http://www.knmi.nl/samenw/campaign_support/CARIBIC/). West of Morocco, a deep convective cloud system associated with a cut-off low lifted the air within a few hours to flight altitude. Approximately fourteen hours later this air was probed by the CARIBIC aircraft. The interesting feature of this cloud affected air is that

Fig. 6. Very low N_{12} particle concentrations in deep convective cloud outflow. These concentrations were measured during the flight on March 7, 2002 between -27.5° and -30.4° longitude and 39.4° and 39.0° latitude. Polluted boundary layer air masses (indicated by high CO, solid circles) were transported from Europe southwest and west into a deep convective cloud system west of Morocco (indicated by trajectories and satellite pictures, *cf.* http://www.knmi.nl/samenw/campaign_support/CARIBIC/), where they were lifted to flight altitude. N_{12} and N_{4-12} concentrations are displayed by the dark grey and light grey areas, respectively, ozone by the solid line.



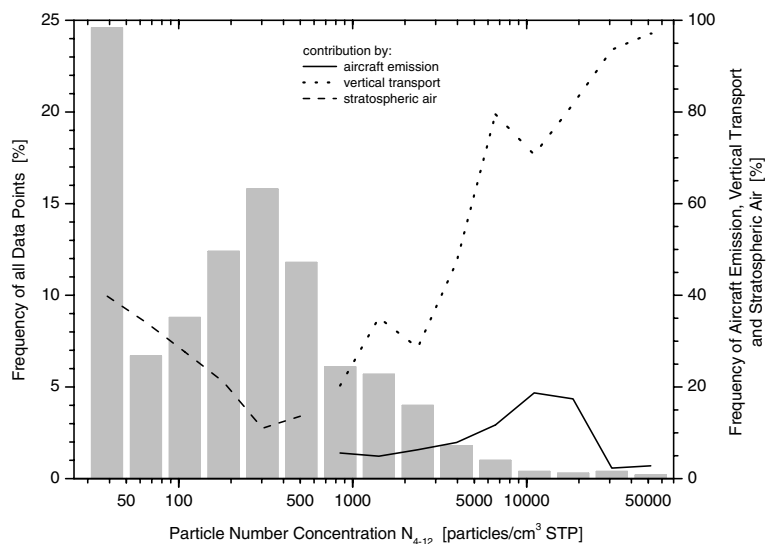


Fig. 7. Histogram of N_{4-12} particle number concentrations for the three CARIBIC flights in March, 2002. Same representation as Fig. 5, however, concentration borders were 50 and 40 000 particles cm^{-3} STP, respectively.

N_{12} values are very low, ~ 200 particles cm^{-3} STP on average, ~ 100 particles cm^{-3} STP at minimum. Note that these concentrations correspond to ~ 66 particles cm^{-3} and ~ 33 particles cm^{-3} at ambient conditions. Such numbers are quite low for continentally influenced air masses and they demonstrate how efficiently deep convective clouds can act as particle filter (Zhang et al., 1998; Martinsson et al., 2000; Schwarzenboeck et al., 2000). Cut-off lows are notorious for their intense precipitation and thus particle scavenging. In the distribution displayed in Fig. 5, approximately one third of all measurements of the lowest bin show an influence of vertical transport. Most cases of cloud outflow measurements in the UT presented in the literature focus on high particle number concentrations caused by these clouds. Here, a case is shown, where the concentrations are initially very low. However, this case still fits into the picture of elevated particle concentrations caused by deep convective clouds, because, as it can be seen in Fig. 6, the reduced particle surface area (low N_{12}) in the respective air mass facilitates the formation of ultrafine particles.

The histogram of the N_{4-12} values for the March flights is shown in Fig. 7 in a similar way as in Fig. 5, however with a broader concentration range. Again number concentrations are lognormally distributed and tailed towards higher values. As for N_{12} , vertical transport dominates in all cases with high number concentrations. On average, 82% of all measurements with N_{4-12} larger than 5100 particles cm^{-3} STP are caused by this process. Aircraft emissions contribute 13% (on average, incl. convective area correction), which is three times as high as for N_{12} . Again, these two processes are the dominant ones, as the sum of both processes account for more than 95% of all high concentration cases. At the lower end of the concentration distribution approximately one third of all measurements are of stratospheric origin. The other measurements likely indicate aged tropospheric air masses.

5. Conclusions and outlook

In this study, we presented particle number and mass concentrations measured in the upper troposphere over the mid-latitude North Atlantic Ocean by CARIBIC. Between May 2001 and April 2002, 22 measurement flights were conducted between Germany and the Caribbean using an automated measurement container on a passenger aircraft. Number concentrations obtained for ultrafine particles and Aitken mode particles were used to calculate probability distributions for summer and winter seasons. Aitken mode particles show a longitudinal gradient in summer with a maximum (mostly 2500–15 000 particles cm^{-3}) over the western North Atlantic close to the North American continent. In winter, concentrations are generally lower and the gradient is smaller. Ultrafine particle distributions are patchier compared to the Aitken mode particle distributions, but again show a maximum over the western North Atlantic in summer. These distributions together with analyses from the literature already indicate that deep vertical transport is an important source process for both kinds of particles. Using the additional information of trace gas mixing ratios, backward trajectories and satellite pictures, an analysis of particle source processes confirms this picture. High particle concentrations ($\gtrsim 8000$ particles cm^{-3} STP) for March 2002 are in about 85% of all cases associated with deep vertical transport and aircraft emissions contribute only 5% (Aitken mode) and 13% (ultrafine mode) to these events. Elemental analysis of the submicrometer particles using PIXE yielded sulphur to be the most abundant element with the highest concentrations, in the range of 4–28 ng m^{-3} STP. The spatial distribution of sulphur mass is in agreement with the findings from the particle number concentration.

In summer 2002, LTU decommissioned the CARIBIC B767-300ER. To continue the measurements, a new CARIBIC system onboard a Lufthansa Airbus A340-600 was constructed

(Brenninkmeijer et al., 2007). It comprises a new container and a novel sampling inlet, including for the first time a video camera and telescopes for a differential optical absorption spectroscopy (DOAS) system. Several new or improved trace gas instruments were included, for example, for O₃, CO, NO/NO_y, H₂O and a 28 sample capacity air sampler. Furthermore, an improved particle sampler (16 channels plus electron microscopy grids) and an optical particle counter for particle size distribution measurements in the size range 0.15–5.0 μm were developed.

On November 13, 2004, the new CARIBIC system had its successful maiden flight from Frankfurt to Buenos Aires. Since May 2005, the system is fully operational and flown once a month on one of the primary routes from Germany to South America or to East Asia. Due to the improved analytical capability of the new system it will be possible to quantify the contribution of different particle source processes in the UT/LS better than before. The CARIBIC aerosol data set will grow and can become a useful tool for the validation of atmospheric models and satellite data as well.

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