Low Ozone and Carbon Monoxide over Central Europe in Air Masses from the Subtropical North Atlantic

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Abstract

The concentrations of ozone and other trace gases observed at high-altitude monitoring stations are characterized by substantial temporal variability. In this study a one-year analysis with the FLEXPART model was carried out, correlating the carbon monoxide measured at the Zugspitze summit (German Alps, 2962 m a.s.l.) with source regions. In particular, a strong correlation of low CO with air masses from the Central Atlantic south of 30°N was found. The same source region has been identified in nearby lidar measurements at Garmisch-Partenkirchen for layers with low ozone. The lidar measurements were now used to find layers that fully hit the Zugspitze summit. The Zugspitze station data reveal low mixing ratios in these subtropical air streams of ozone (20-30 ppb), carbon monoxide (about 60 ppb) and NO_y (0.03-0.4 ppb). These values match the mixing ratios reported for the background subtropical Atlantic. The advection from low latitudes is crudely estimated via trajectory analyses to lower the ozone mixing ratio in the free troposphere over Central Europe by 7 to 8 ppb. It is concluded that during the rather long transport to Europe the concentrations are almost unchanged by photochemical processes or mixing with surrounding air. Low free-tropospheric mixing became even more evident in the case of a very dry layer with more than 80 ppb of ozone that propagated above the clean subtropical air mass from the African West coast to Europe via the Western Atlantic and that was most likely fed by a stratospheric air intrusion more than twenty days prior to the arrival over Garmisch-Partenkirchen. These observations confirm our recent findings for direct stratospheric air intrusions that frequently exhibit almost negligible relative humidities even in rather thin layers. The consequence is a major challenge for numerical models which quite frequently overestimate atmospheric mixing due to their limited spatial resolution and the required parameterizations.

1 Introduction

Prefrontal advection from low latitudes has been shown to result in very low mid-latitude ozone values close to those observed in the southern hemisphere (e.g., Bethan et al., 1998; Eisele et al., 1999; Grant et al., 2000; Carnuth et al., 2002; Trickl et al., 2003; Roelofs et al., 2003a). For Central Europe, the region of interest in this study, the Central Atlantic roughly between 30º W and 65º W and south of 30º N seems to be the main source region for low ozone. Transport from the subtropical Atlantic to Central Europe mostly occurs in warm conveyor belts over the Central Atlantic, and these air masses may be considerably humid (Bethan et al., 1998; Trickl et al., 2003). An alternative pathway for low-ozone advection from the subtropical Atlantic was reported on by Carnuth et al. (2002). Here, the prefrontal rise occurred directly over the Mediterranean Sea and the Alps during a Föhn event (with Saharan dust) and was preceded by westerly flow from the subtropical Atlantic over Africa at about 20º N (Carnuth et al., 2002).

Ozone mixing ratios over remote oceanic regions may, indeed, be rather low. In particular, values of about 10 ppb (and less) have been observed in the marine boundary layer (MBL) of the remote Pacific and Indian Oceans, caused by long isolation of these air masses from ozone precursor sources and, thus, prolonged photochemical ozone decomposition under low-NO_x conditions (e.g., Oltmans and Levy, 1992; Singh et al., 1996; Kley et al., 1996; Browell et al., 1996; Rhoads et al., 1997; Browell et al., 2001). The near-surface mixing ratios over the tropical and southern Atlantic are somewhat higher (with the exception of the Inner-Tropical Convergence Zone), which might be ascribed to the shorter distance to the adjacent continents and their emission sources. Weller et al. (1996) reported near-surface ozone values of 15 to 25 ppb in the southern hemisphere during several ship cruises along the Atlantic, in reasonable agreement even with the values for the South African coastal station Cape Point (Oltmans et al., 2006; Brunke et al., 2009), but 22-25 ppb between the equator and 20º N during a passage in late autumn1991, and roughly 40 ppb north of the equator in the other cases. However, the ship passed the northern tropics and subtropics rather close to the African continent. Over the eastern subtropical Atlantic the influence of continental emissions and also some European impact cannot be neglected (e.g., Rodríguez et al., 2004). Nevertheless, similar findings were reported by Lelieveld et al. (2004) and Smit (2004) from cruises along roughly the same pathways in the northern hemisphere. Kley et al. (2007) analysed ozone and relative humidity for six years of MOZAIC (Measurements of Ozone by Airbus In-Service Aircraft; Marenco et al., 1998) flights, again rather close to the African coast. For outflow from deep convection, ozone histograms peaking at 30 ppb were obtained, presumably related to updraft of air from the MBL. Further to the north, at the Pico station on the Azores (38º N, 28º W, 2.2 km a.s.l.), ozone is also between 20 and 30 ppb under background conditions (Val Martin et al., 2006; at this station also North American influence has been observed). Reeves et al. (2002) found 10 to 30 ppb of ozone during two flights south and southwest of the Azores.

The situation does not change much to the west (e.g., Oltmans and Levy, 1992; Dickerson et al., 1995; Gouget et al., 1996; Thompson et al., 2000), but with a tendency towards lower values as one approaches the Caribbean Sea. Observations in Bermuda in 1992 showed 15 (±2) ppb of ozone in so-called marine air and 35 (±5) ppb in “local” air (Dickerson et al., 1995). Measurements in Barbados around 1990 revealed monthly means of O_3 even varying between 15 ppb (August) and 29 ppb (January) (Oltmans and Levy, 1992). The summer

minimum can be seen as a consequence of the photochemical ozone destrucion over the ocean (e.g., Ayers et al., 1992). In summary, 20 to 30 ppb appears to be the typical range of background ozone mixing ratios over the subtropical North Atlantic.

As to carbon monoxide, the lowest mixing ratios, roughly 35 ppb (local summer) to 80 ppb (local winter), are, again, reported for the remote Pacific and Indian Oceans (Fraser et al., 1986; Khalil and Rasmussen, 1988; 1994; Allen et al., 1996; Rhoads et al., 1997; Duncan et al., 2007; more complete series: http://www.esrl.noaa.gov/gmd/ccgg/iadv/). At Cape Point the mean annual CO was rather constant until 2000 (about 53 ppb), followed by a decline to 46 ppb afterwards (Scheel et al., 1990; Brunke et al., 2009). Similarly low values are not reached at low latitudes over the subtropical North Atlantic where 60 ppb and higher values have been observed under background conditions during the warm season (e.g., Gouget et al., 1996; Thompson et al., 2000; Penkett et al., 2004; Owen et al., 2006; Val Martin et al., 2006).

In this paper, we discuss aspects of these rather frequently observed subtropical air masses in some more detail. We first present two case studies based on ozone sounding with the differential-absorption ozone lidar at Garmisch-Partenkirchen (German Alps) and in-situ measurements at the nearby Zugspitze high-altitude station (2962 m a.s.l.). Then, the principal source regions of high and low Zugspitze CO are evaluated by transport modelling for a full year (2000). Finally, we describe some climatological evaluation of the subtropical air masses based on 2.5 years of backward trajectories.

2 Methods

2.1 Measurements

In this study we use data from measurements with the tropospheric ozone lidar at IMK-IFU (47º 28' 37" N, 11º 3' 52" E, 740 m a.s.l.). This lidar was completed in its first version in 1990 (Kempfer et al., 1994) and upgraded in 1994 and 1995 (Eisele and Trickl, 1997; 2005). It has a unique vertical range between 0.2 km and roughly 15 km above the ground, features low uncertainties of about ±3 ppb in the lower troposphere and ±6 ppb (under optimum conditions) in the upper troposphere. The upper-tropospheric performance may be degraded in the presence of high lower-tropospheric ozone concentrations absorbing much of the ultraviolet laser emission and by enhanced sky light in summer, in particular in the presence of clouds. The vertical resolution is dynamically varied between 50 m and a few hundred metres, depending on the signal-to-noise ratio that decreases with altitude. The lidar has been used in numerous investigations mostly focussing on atmospheric transport (e.g., Carnuth et al. 2002; Eisele et al., 1999; Stohl and Trickl, 1999; Seibert et el., 2000; Zanis et al., 2003; Trickl et al., 2003; 2010a; 2010b).

In addition, in-situ data from the monitoring station Zugspitze (2962 m a.s.l.) are used, in particular ozone, carbon monoxide, NO_y and relative humidity (RH). Ozone has been measured since 1978 (e.g., Reiter et al., 1987; Scheel et al., 1997; Oltmans et al., 2006). A chemiluminescence instrument (Bendix 8002, Bendix Corporation, U.S.A.) was in operation until 1999. Thereafter, only ultraviolet absorption instruments have been employed (TE49 analysers, Thermo Electron, U.S.A.). Carbon monoxide has been measured since 1990, using instrumentation based on gas chromatography with a mercury reduction detector (RGD2, Trace Analytical, U.S.A.) or gas filter correlation infrared absorption (TE48S, Thermo Electron, U.S.A.) as well as vacuum resonance fluorescence (AL5001, AeroLaser, Germany),

with two different systems running in parallel for most of the time. During recent years, nitrogen oxides at Zugspitze were measured with an analyser equipped with a molybdenum converter (Thermo Environmental Instruments, type TE42-C). RH is measured with a dew-point mirror (Thygan VTP6, Meteorolabor, Switzerland) with an uncertainty below 5 % RH.

2.2 Models

The transport pathways and source regions were identified by calculations with the FLEXTRA trajectory model (Stohl et al., 1995; Stohl and Seibert, 1998) and the FLEXPART particle dispersion model (Stohl et al., 1998; Stohl and Thomson, 1999; Stohl et al., 2005). Both models used ECMWF three-dimensional meteorological fields with three-hourly temporal, 1×1-degree horizontal and 60-level vertical resolutions.

For long transport paths trajectory analyses become less meaningful due to an increasingly bad representativeness and the neglect of turbulent mixing. As a consequence backward options of the FLEXPART model have been developed and sucessfully applied (e.g., Stohl et al., 2003; Trickl et al., 2003; Huntrieser et al. 2005). The backward plumes yield a much more complete picture of where the air masses come from (Stohl et al., 2002). Several products can be derived from the model simulations. The first product is a column-integrated emission sensitivity which is proportional to the residence time of the particles over a unit area. Longer residence times mean a higher sensitivity to local emissions. Emission sensitivities in a 100-m deep footprint layer, which is nearly always located inside the planetary boundary layer (PBL) can identify areas of potential emission uptake from the surface. Turbulence and convection in the PBL as well as moist convection throughout the atmosphere are accounted for in the FLEXPART model (Stohl et al., 2005; Forster et al., 2007). By folding the emission sensitivity with emission fluxes from appropriate inventories, geographical maps of source contributions can be calculated. For the work presented here the EDGAR 3.2 fast-track inventory for the year 2000 (Olivier and Berdowski, 2001) has been used. For large parts of North America, the regional inventory of Frost et al. (2006) was used in the most recent simulations (see below). By integrating the source contributions over individual continents, total continental contributions are obtained as emission tracer mixing ratios. Other products include graphical displays of a cluster analysis of particle trajectories as described by Stohl et al. (2002) and the fraction of particles residing in the PBL and above the tropopause (defined here as 2 potential vorticity units) as a function of time.

FLEXPART backward simulations were carried out for 50 250-m altitude bins above Garmisch-Partenkirchen, up to 12.5 km a.s.l.. Thus, transport pathways can be analyzed as a function of arrival altitude. For instance, the vertical distribution of emission tracers with origins from different continents can be displayed. For a statistical analysis of source regions of the carbon monoxide observation at the Zugspitze summit in the year 2000, we performed forty-day backward simulations. For each single three-hour interval during the entire year 2000, 20000 particles at a time were released in a box domain around the Zugspitze summit and integrated backwards in time for fourty days. The box domain had a dimension of 400 m in height, 0.2°× 0.2° in the horizontal and three hours in time. The particles were initially spread evenly throughout this 4D space.

For a visualization of stratospheric intrusions an approach was applied that has routinely been used for intrusions warnings since the STACCATO project (Influence of Stratosphere-Tropo-

sphere Exchange in a Changing Climate on Atmospheric Transport and Oxidation Capacity; STACCATO, 2003; http://www.forst.tu-muenchen.de/EXT/LST/METEO/staccato/). Daily four-day trajectory calculations, based on operational ECMWF forecasts, have been provided to the STACCATO partner stations by ETH Zürich (e.g., Zanis et al. 2003; Trickl et al., 2010a). The trajectories are calculated with the Lagrangian Analysis Tool (LAGRANTO; Wernli and Davies, 1997), starting in the entire region covering the Atlantic Ocean and Western Europe (20º east to 80º west and 40º to 80º north) between 250 and 600 mbar. From this large set of trajectories those initially residing in the stratosphere (potential vorticity larger than 2 pvu) and descending by more than 300 mbar into the troposphere during the time period covered are selected as "stratospheric intrusion trajectories".

In the present study, trajectories images were prepared every six hours for the period July 20 to August 30, 2000, that precedes the beginning of the forecasts for STACCATO. For a few days specified in Sec. 2.3 the trajectories were extended to six days.

3 Case studies

July 21-23, 2001

The ozone layering during the early phase of high-pressure periods at our site during the warm season have been found to exhibit reproducibly a three-layer structure as shown in Fig. 1 (Eisele et al., 1999; Trickl et al., 2003; Trickl et al., 2010b). The lowest layer (high ozone) is caused by a stratospheric air intrusion. Above this, low ozone from the subtropical Atlantic is observed, followed typically above 4 km by air with elevated ozone from across the Atlantic. As analysed by Trickl et al. (2010b) some of the high-ozone layers also contain air from even more remote source areas, notably the stratosphere along the subtropical jet stream and the East Asian PBL.

The subtropical air, after some considerable prefrontal rise, joined the main flow between North America and Europe and subsequently proceeded towards Central Europe on an almost straight path, in contrast to the anticyclonic subsidence seen in other cases (Fig. 2). This case is special since the subtropical layer could be fully observed at the Zugspitze summit (Fig. 3), with minimum ozone and carbon monoxide mixing ratios of 23 ppb and 53 ppb, respectively. As in the "classical" May-1996 case (Eisele et al., 1999; Trickl et al., 2003) the relative humidity of the subtropical air is high. In addition, the NO_y values are just 0.03 to 0.1 ppb which is lower than in the stratospheric intrusion at the beginning of the observational period of the lidar. Finally, the minimum CO values range around 53 ppb, which is lower than the values mentioned for the subtropical Atlantic in the introduction. It equals the annual average observed at the Cape Point station in the southern hemisphere before 2000 (Brunke et al., 2009).

September 8 to 12, 2000

The quite analogous lidar measurements between September 8 and 11, 2000, had not been fully understood in our first analysis (Trickl et al., 2003). The ozone series is displayed in Fig. 4 and, again, shows the rather typical three-layer structure for beginning high-pressure periods. The three layers of principal interest are L1 (between 4 and 6 km at the beginning, later lower), L2 (between 4.5 and 6 km) and L3 (between 8 and 10 km). L1 is the typical low-

ozone subtropical layer. L3 was mainly caused by ozone import from the south-eastern U.S. on September 8 and early September 9, later from the Pacific (Trickl et al., 2010b).

As in the July-2001 case, the low-ozone layer (L1) fully descended to the Zugspitze altitude and below. The Zugspitze data (Fig. 5) show a short drop in ozone (to 32 ppb) and CO (to 68 ppb) simultaneous to a rise in RH to 66 % during the first hours of September 10. A similar situation is found in the afternoon of that day, at the time marked by the second arrow in Fig. 5. The vertical distribution in Fig. 4 shows that the low-ozone layer expanded upwards in the afternoon to the Zugspitze altitude level, which confirms this observation at the summit station. Also the NO_y values at the two times of minimum ozone marked by arrows in Fig. 5 (0.5 ppb and 0.2 ppb, respectively) are somewhat higher than in the first case, possibly due a slightly enhanced level of mixing of surrounding air into the rather thin layer.

The air mass corresponding to Layer L2 between 4.5 and 6 km follows almost the same pathway from the subtropical Atlantic to Europe. As a consequence, the high ozone mixing ratios up to 85 ppb are difficult to understand which stimulated some extra analysis effort, described in the remaining part of this section.

In order to get some idea about the origin of the elevated ozone we carried out a twenty-day FLEXPART backward simulation. Results for the altitude bin between 5.75 and 6.0 km are shown in Fig. 6 and show low North American influence. The backward plume, on average, stays above 4 km, i.e., outside the PBL. Next to the African coast some branching occurs indicating some separation into an African and a northerly component the centre of which can be followed to about 50 N, roughly south of Iceland.

The results do not any overlap with polluted regions. We, therefore, extended the FLEXPART simulation to forty days. The result (not shown) hardens the two branches indicated in Fig. 6. The African branch is mainly located between 10° and 20° N, with minor extensions to the Mediterranean Sea, and leads back to Arabia and, to some extent, India (compare, e.g., Roelofs et al., 2003b). However, for both branches, no significant PBL contact was found over continents, the calculated vertical distribution of (exclusively European) emissions arriving above the lidar position exhibiting a pronounced minimum between 4 and 6 km, the range of layer L2.

The missing PBL contact reduces the number of possibilities to explain the elevated ozone in layer L2. One explanation could be tropical biomass burning in Africa, but this is not that likely in this latitude range in August and, indeed, not verified in the fire map for August 2000 (http://tsdis.gsfc.nasa.gov/tsdis/Fire/Images/MonthlyArchive/200008.fire.gif). Another possibility is ozone formation due to NO_x produced by lightning. The satellite images provided for our earlier publication (Trickl et al., 2003) show pronounced local convective activity during the entire first week of September, over the south-eastern U.S., over the adjacent region of the Atlantic and over the Caribbean Islands. Also, lightning-induced African contributions on the concentrations in layer L2 could be thought of (e.g., Sioris et al., 2007; Schumann and Huntrieser, 2007). The satellite lightning maps of the relevant period in August 2000 (http://thunder.msfc.nasa.gov/lis/), indeed, show a multitude of lightning observations to latitudes even higher than 20º N, between the west coast and more than 30º E.

An inspection of the radiosonde data in and around the Alps for the relevant period around September 9 reveals for layer L2 rather low humidity with minimum values below 5 % which

seems to exclude significant contributions from deep convection. Thus, we favour the third and perhaps most important possibility, ozone import from the stratosphere, in particular within the branch of the backward plume leading to higher latitudes. However, the forty-day FLEXPART run did not yield a clear answer. The mean vertical plume position ascends to just 6 km in both branches, the stratospheric fraction growing to just 6 %. This is significant, but yields just a moderate increase in ozone of the order of 30 ppb. By contrast, LAGRANTO intrusion forward trajectories calculated for the period July 20 to August 30 revealed two intrusions descending southwards from the arctic towards the African west coast. For the more suitable of these two periods, August 16 to 18, the trajectory calculations were extended to six days for obtaining a better view of the outflow to the subtropics. One example from the most relevant part of this time period is displayed in Fig. 7. There is some evidence of the formation of low-level southward flow of a part of the intrusion along the African coast (below 2 km). Additional trajectory calculations (not shown) demonstrated a subsequent westward turn as indicated in the FLEXPART results. This kind of turn of intrusion air masses was discussed by Rodriguez et al. (2004) in their analysis of the measurements at Izaña, Tenerife (28.309 N, 16.499 E, 2373 m a.s.l.). Indeed, the ozone and relative-humidity data for Izaña verified the passage of the intrusion in the vicinity of that station during the period August 24 to 27, 2000 (Y. González Ramos and E. Cuevas-Agulló, personal communication, 2011). The maximum ozone mixing ratio, 73 ppb (typical background values being roughly 30 ppb), was reached around midnight between August 24 and 25, when the humidity (20 %) was far from its minimum (4 %). This suggests just some partial overlap with the stratospheric air mass, which would be necessary for explaining the lower ozone values with respect to those obtained with the lidar from this source alone.

We did not spend much effort for analysing further the eastward branch in the FLEXPART in the FLEXPART results. It is reasonable to assume that this air mass was sufficiently dry in order not to raise the relative humidity in the combined air stream too much.

4. One-year Simulation of CO for the Zugspitze Summit

The mixing ratio of carbon monoxide observed at the Zugspitze summit varies strongly as a function of the air-mass origin. As an example we show in the upper panel of Fig. 8 time series for the year 2000. The highest CO values are usually observed in frontal systems, due to the presence of polluted PBL air, and are accompanied by very low ozone. Frontal passages preceded the high-pressure periods presented in Figs. 1 and 4 for July 20, 2001 and September 7, 2000, respectively. However, in these cases the increase in CO was quite limited (due to overpassing moderately polluted regions of Europe in both cases). A very pronounced increase of CO for such a situtation on November 13, 2001, is seen in Fig. 9 of (Trickl et al., 2010a). Here, the air mass overpassed Great Britain and East Germany at low altitude.

The low-ozone layers examined in the two case studies in Sec. 3.1 are also low in CO. This situation of beginning anti-cyclonic conditions is one of the important situations for low CO at the Zugspitze summit. In order to obtain a more general insight into the relevant source regions of CO, a statistical analysis of the FLEXPART model output for the Zugspitze summit in combination with the CO measurement data was made for the year 2000. The half-hourly averages of Zugspitze CO were binned into three-hourly mean values for matching the time resolution of the model data (upper panel of Fig. 8; note that the September minimum corresponds to the episode in Fig. 4). In order to remove the slow seasonal variation of this

time series and to concentrate on synoptic-scale variability, the data were normalized relative to thirty-day running means, as illustrated in the lower panel, of Fig. 8. The FLEXPART output was then sorted according to the normalized measured CO values and the average emission sensitivities for the 10 % highest and 10 % lowest CO values are used to display the monthly air mass origins for these extreme measured values.

The resulting mean emission sensitivities can reveal where air masses arriving at the Zugspitze summit had been typically residing during the preceeding weeks, for the total data set as well as for the highest and lowest 10 %, respectively. Fig. 9 shows the monthly mean emission sensitivities for three different altitudes and for the total column for all air masses arriving at the Zugspitze during January and July 2000. In both seasons, the predominantly westerly flow leads to a preponderance of residency in the western hemisphere. However, the typically higher wind speeds in winter than in summer result in a much quicker mixing of particles throughout the northern hemisphere in wintertime. This is especially noticeable at low altitudes, where, in July, residence in Western Europe and the nearby Atlantic is strongly dominant. Even after forty days, inter-hemispheric exchange appears to be largely insignificant.

If the global residence time distribution for the highest 10 % of CO values is compared to that for the lowest 10 % of CO values, for any particular month, very clear differences in the typical source regions emerge. Figures 10 to 12 show sets of panels for the total atmospheric column, 250 m and 5 km altitude, respectively, picked from four different seasons. The corresponding panels for 12 km are not shown here, but can be accessed in the ATMOFAST final report on page 101 (ATMOFAST, 2005). The emission sensitivity first grows with altitude, a fact that can also be concluded from Fig. 9, and then decrease towards the tropopause region. The role of CO in the tropopause region will be discussed further in a subsequent publication on water vapour, ozone and CO in stratospheric intrusions.

In winter, for air masses which have resided at low altitude at some stage (Fig. 11), low-CO air is largely sourced in the tropics and sub-tropics, while high-CO air typically has traversed near the surface in the northern extratropics. The source distributions in the middle free troposphere (Fig. 12) also reveal a typical „clean-air“ pathway curving from the subtropical Atlantic via western Europe. This is in some agreement with the expectations from the lidar case studies. The panels for April and October also show contributions to low Zugspitze CO from North Africa. From this material we cannot distinguish how much of these contributions are due to prefrontal advection over the Mediterranean Sea or due to long-range transport from Africa towards the Caribbean Sea and then back to Europe.

In contrast, high-CO air masses are typically sourced further north, being advected rapidly from the mid-troposphere across Canada on the poleward side of the north Atlantic jet. In summer, when the large-scale wind flow is generally weaker, a much greater European influence is seen throughout the troposphere. Typically, high-CO air has resided over Europe itself, whereas low-CO air has spent more of its time over the oceans, especially the suptropical North Atlantic.

5. Statistical Analysis of Low-latitude Air Based on 2.5 Years of Backward Trajectories

FLEXTRA eight-day backward trajectories with vertically stacked arrival altitudes above Garmisch-Partenkirchen at 3-h intervals were calculated for the period April 2003 to September 2005. The trajectory plots were used for characterizing the influence of the most important source regions and for classifying the routes of trans-Atlantic transport (ATMOFAST, 2005; a separate publication is planned). Short gaps in the trajectory plots were filled with trajectory plots obtained from other sources. These periods were found not to be relevant for the study presented here. We selected the results for 0:00 UTC and 12:00 UTC out of the large number of plots and, thus, reduced the overall number of times to 1826.

Here, we focus on the statistics obtained for the trajectories that arrive from the tropical and subtropical North Atlantic (south of 25º N and between 20º W and east of North America; the cases between 25° N and 30° N were weighted with 0.5). It turned out that the fraction of trajectory plots showing (sub)tropical influence in the free troposphere above Garmisch-Partenkirchen was as high as 27.3 %. There is no strong variation of this fraction with season (i.e., April – September compared with October – March).

The altitude distribution of the average arrival height of individual trajectory bundles exhibits some significant structure (Fig. 13). The lowest subtropical contribution is seen at low altitudes, in some agreement with the idea of prefrontal rise of these air masses being included in the transport to Europe. There layers with elevated occurrence of advection from the PBL over the subtropical Atlantic are indicated (2.5 – 6 km, 6 – 10 km, 10 – 11.5 km). Figure 13 also shows the results for anti-cyclonic and cyclonic arrival of the subtropical trajectories over Garmisch-Partenkirchen. 62 % of the trajectories that could be traced back to the PBL over the low-latitude Atlantic exhibit anti-cyclonic behaviour and just 38 % arrive on a cyclonic pathway, in contrast to the almost equal fractions found for trans-Atlantic transport. There is also a difference in the altitude distribution: In the upper troposphere the anti-cyclonic contributions prevail.

The highest and lowest layers are understandable from the observational data, with ozone minima in the lower (see Sec. 3.1) and the upper free troposphere, whereas the central, rather thick layer cannot easily be explained at present. The cyclonic trajectories frequently indicate prefrontal lifting over the Mediterranean Sea and Europe. In some similarity to typical arrival heights of Saharan dust over Garmisch-Partenkirchen, resulting from a similar prefrontal rise, lower altitudes are reached (e.g., Jäger et al., 1988; Papayannis et al., 2008). Still, the altitudes for the middle layer indicated in the blue histogram in Fig. 13 reach more than 8 km, whereas dust layers are mostly confined to altitudes below 6 km.

Despite the low number of counts a seasonal dependence of the trajectories exhibiting subtropical influence was evaluated (Fig. 14). An astonishing difference between the period October – December and January – March was found, with a change from a low to a pronounced upper-tropospheric component: Both groups of months belong to the colder part of the year!

The advection of air with 20 to 30 ppb of ozone from low latitudes significantly reduces the average ozone mixing ratio in the free troposphere. For instance, when assuming an annual mean value of 50 ppb, and 25 ppb in subtropical air, the reduction of the annual mean would

be 7.8 ppb. Even if one excludes the central part of the distribution between 6.0 and 9.5 km, for which we do not have sufficient information on ozone, one obtains a lowering by 7.1 ppb.

6. Discussion and Conclusions

The ozone measurements with the lidar at Garmisch-Partenkirchen have revealed cases in which moist low-ozone subtropical air masses fully overlap with the nearby Zugspitze summit, allowing for a quantitative analysis of some of the relevant trace gases in such an air stream. Full overlap is not generally the case. One counter-example was published for June 2001 for a similar kind of observation as in the first two subchapters of Sec. 3.1 (Zanis 2003; Trickl, 2010a). In this case the lidar minimum O_3 was 34 (±3) ppb, located around 3400 m, but 40 ppb were registered at the Zugspitze summit, at the edge of the subtropical layer. Another extreme, very high CO and almost negligible ozone, may occur during the frontal passage preceding such a period of transition to an anti-cyclonic situation (see first paragraph of Sec. 3.2). This leads to quite drastic variations in concentration for both species during periods of just two or three days.

The model calculations in this paper verify a correlation of the low-CO events with the subtropical source region. Our results are in some agreement with data by Bethan et al. (1998). During an aircraft mission in 1994 they observed low to moderate O_3, CO and NO_y (36 ppb, 120 ppb, and 0.5–0.6 ppb, respectively) and RH ≈ 90 % in the outflow of a WCB over the south-western part of the United Kingdom which they also traced back to the PBL over the subtropical Atlantic.

Important questions are: what generates the low concentrations of ozone and carbon-monoxide over the remote North Atlantic, and why are they more or less conserved during a long-range transport over thousands of kilometres? The subtropical North Atlantic is surrounded by a number of important emission sources that could contribute to some higher background concentrations. The air inflow into the PBL over the subtropical North Atlantic is likely to be dominated by the trade winds. As a consequence, African emissions should be most important, some contributions from the Eastern Mediterranean Sea or even further to the east (Roelofs et al., 2003b) could occasionally be present after long-range transport via the southern half of the Sahara desert. African emissions in the northern hemisphere are limited to 0º to 10º N, also during the biomass burning season around January (Edwards et al., 2003; Gros et al., 2004). It is interesting to note that for 0° even to about 40° N there is a positive ozone trend obtained from for ship cruises not too far from the African coast since the mid-seventies (Lelieveld et al., 2004), from 23 to more than 30 ppb on average, indicating the growing role of African emissions.

Satellite images shown by Edwards et al. (2003) and Gros et al. (2004) suggest that even during periods of emission outflow from tropical and subtropical Africa the CO concentrations decrease towards the Caribbean Sea where they reach values around 80 ppb. CO may be expected to decline during slow transport in the moist MBL, at least by reaction with OH (e.g., (Taylor et al., 1996) and references therein). Values around 80 ppb are also typical of summer-time background conditions at or south of the Azores (Penkett et al., 2004; Val Martin et al., 2006). The CO mixing ratios around 55 ppb seen in the Zugspitze data for July 23, 2001, correspond to the lowest summer-time values seen at the Pico station, but could also imply some additional decomposition in that moist air mass on the way to Central

Europe. The ozone mixing ratios from observations over and around the subtropical Atlantic are between 10 and 40 ppb and almost match the range of values (20 to 40 ppb) observed over Garmisch-Partenkirchen in the air masses from this region. The pathway for this kind of transport in the cases studied is anti-cyclonic and, therefore, less likely to be influenced by inflow of North American air pollution.

The region from where our low-O_3, low-CO air masses come from is part of the broadest part of the North Atlantic, where the influence of the surrounding sources of air pollution should be the lowest and chemical depletion of these species during the relatively slow near-surface transport (5 to 10 m s^{-1}) can dominate. Reeves et al. (2002), who found NO levels of typically 10 ppt and less during their flights around the Azores at altitudes below 5 km, determined "NO compensation points" of 12 to 33 ppt. For conditions of low NO_x (i.e., below the compensation point) ozone depletion takes place that is, e.g., caused by reaction with water vapour or peroxy radicals (e.g., Crutzen, 1973; Chameides and Walker, 1973; Liu et al., 1983; Davis et al., 1996; Kley et al., 1996; Reeves et al., 2002). There is also increasing evidence that halogen chemistry contributes to the ozone loss in the MBL (e.g., Chameides and Davis, 1980; Davis et al., 1996; Dickerson et al., 1999; Allan et al., 2000; Platt and Hönninger, 2003, Carpenter, 2003, Smythe-Wright et al., 2006; Whitehead et al., 2010; McFiggans et al., 2010; Furneau et al., 2010). Smythe-Wright et al. (2006) report on up to 100 ppt of CH_3I over the North Atlantic south of 25º N, most likely released by prochlorococcus algae. No similar latitudinal effect was found for $CHBr_3$ and CH_2Br_2 (Carpenter et al., 2009).

For the range above the marine surface layer Helmig et al. (2008) also concluded photochemical destruction from their analysis of the measurements at the Pico station (2225 m a.s.l.) on the Azores. The ozone depletion in continental air masses arriving at this station is the strongest for slow transport. The NO_y values reported for the Pico station (Val Martin et al., 2008) are higher than those shown in Fig. 3 for July 23, 2001 (roughly 0.2 to 0.5 ppb for July), but those for marine conditions in Bermuda, 0.15 ppb (Dickerson et al., 1995), are rather close. For comparison, the background NO_y values observed in air from the remote Indian Ocean are also of the order of 0.15 ppb (Rhoads et al., 1997). However, the NO_y values in Fig. 3 are perhaps just indicative of the general nature of these air masses since removal of NO_y from the air travelling from the subtropics to Europe cannot be excluded.

Above the MBL elevated ozone concentrations may persist. In the September 2002 case we found an elevated-ozone layer that had travelled parallel to the low-O_3 air below it from the African coast to the West Atlantic, staying at elevated altitudes all the time. A stratospheric intrusion to the east of Greenland was concluded to be an important source of the additional ozone. In addition, long-range transport from Arabia and beyond via the southern Sahara was found to contribute to that layer (L2), resembling the transport of the plume from the Kuwait oil fires in July 1991 to Garmisch-Partenkirchen (Carnuth et al., 2002; the full corresponding aerosol time series was recently published by Fromm et al., 2010 (Fig. 6)). This branch rise backward to about 6 km towards the east, but potential contact with the stratosphere was not attempted to verify.

The observations of low-O_3 subtropical air are not limited to the lower free troposphere. Our trajectory analysis shows that subtropical influence occurs almost all the way up to the tropopause and, therefore, should have a significant influence on the ozone budget over our measurement site (a lowering by 7 to 8 ppb). Upper tropospheric ozone minima are rather

frequently seen in our data. We found that these minima are often associated with the outflow of WCBs and co-exist with cirrus clouds. Sometimes the measurements with the ozone DIAL have shown even near-zero ozone concentration in these layers. The classical example of this kind was published by Reichardt et al. (1996), but their trajectories were too short for an identification of WCB outflow. Speculations on ozone destruction in cirrus clouds were raised. We repeated the trajectory analysis for this case and clearly found WCB-based air-mass lifting from the Caribbean Sea, thus eliminating the need for invoking heterogeneous decomposition as an explanation of the ozone loss. Davies et al. (1998) found a similar case with almost zero ozone (RH ≈ 55 %), but ascribed this observation to import from the tropical Pacific without the presence of cirrus clouds. Indeed, over the tropical Pacific Kley et al. (1996) found very low ozone even in the upper troposphere under convective conditions.

From our results we conclude low air-mass mixing with adjacent layers during the transport from low latitudes to Central Europe (and in the case of the high-ozone layer on September 9 to 10, 2000, from even significantly beyond this region). Very low mixing was recently also rather consistently found for stratospheric air intrusions reaching our measurements site from arctic regions (see (Vogelmann and Trickl, 2008) for an example of a particularly thin intrusion layer with a relative humidity of about 1 %). Low mixing is also concluded from the rather steep concentration gradients within the layer boundaries. Part of the explanation is that both the layer itself and the surrounding air masses proceed with similar wind speeds and the lack of vertical wind shear limits turbulent exchange. We conclude that mixing mostly occurs in the vicinity of frontal systems. The subtropical layers are obviously lifted far enough ahead of the front for an inflow of other air masses to occur. This has important implications for the simulation of such features (Stohl et al., 2004), particularly in Eulerian chemistry-transport models, which would artificially disperse long-lived features too rapidly (Rastigejev et al., 2010).

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Figures:

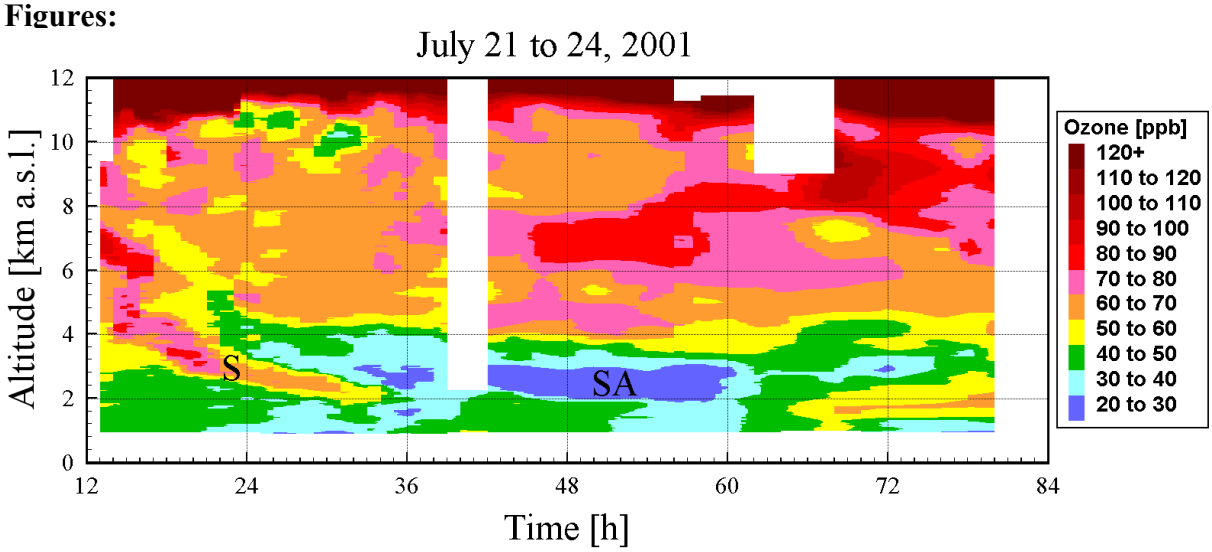

Fig. 1. Ozone sounding series in July 2001 at the beginning of a high-pressure period; S marks a stratospheric air intrusion, SA air from subtropical Atlantic, the layers above 4 km are due to long-range advection from North America and beyond as discussed in (Trickl et al., 2010b). The time scale is given with respect to 0:00 CET (Central European Time, = UTC + 1 h), on July 21.

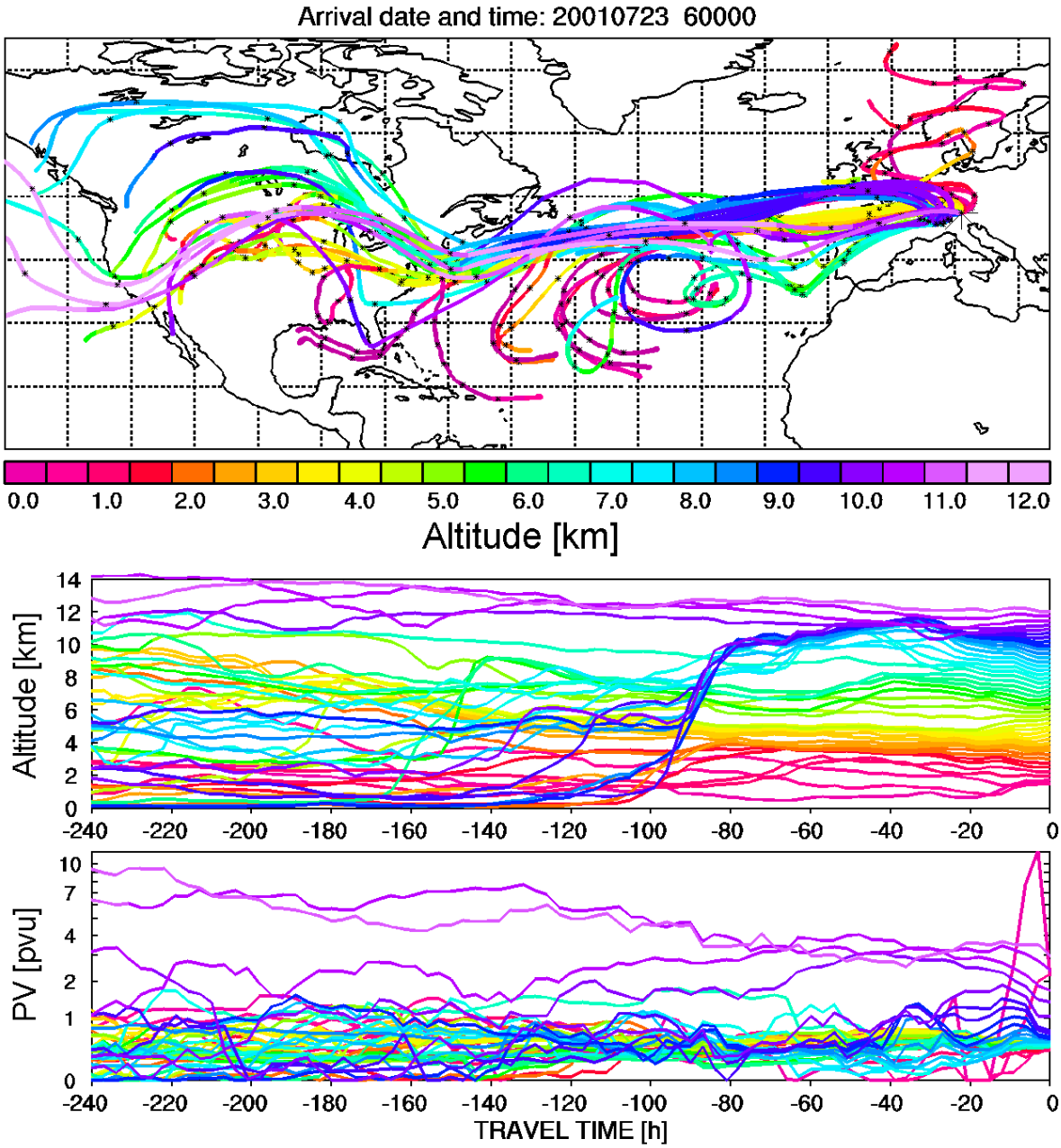

Fig. 2. Ten-day FLEXTRA backward trajectories intiated above Garmisch-Partenkirchen on July 23, 2001, at 6:00 UTC (7:00 CET); the altitude [km] is colour coded, in the upper panel at the horizontal position of the trajectories shown, in the central and bottom panels according to the absolute altitude of the trajectory over Garmisch-Partenkirchen.

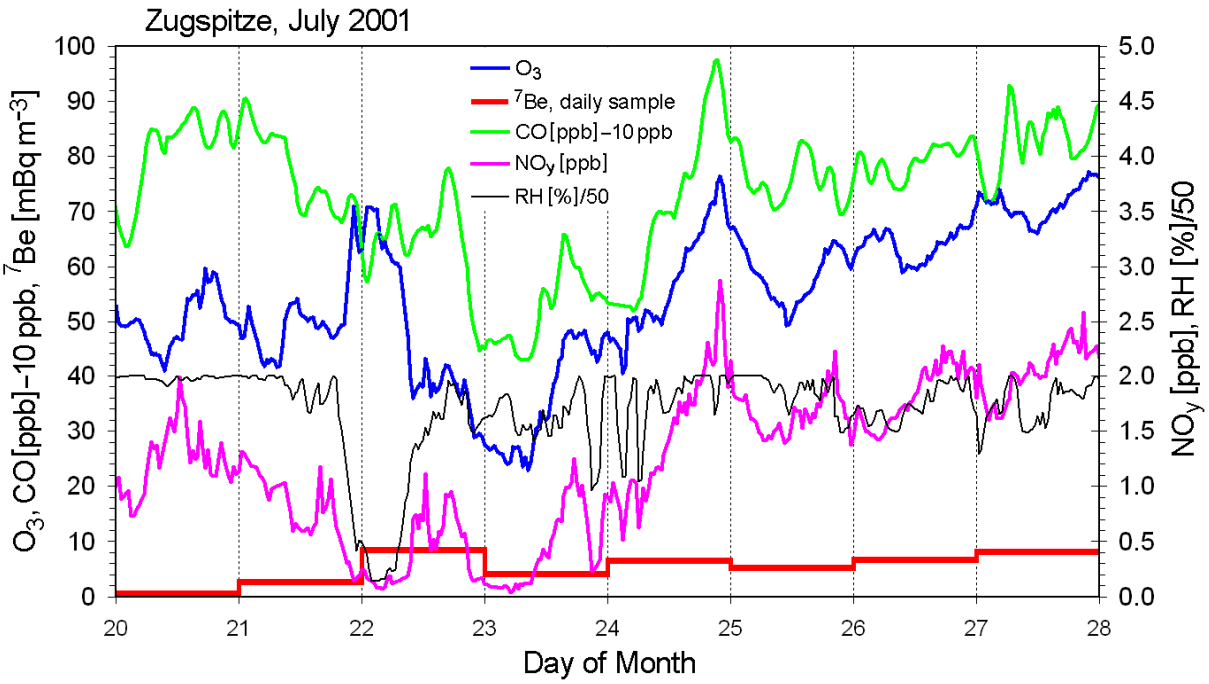

Fig. 3. Zugspitze summit, July 20 to 27, 2001 (CET): ozone, CO, NO_y, relative humidity (RH) and ^7Be; the air masses from the subtropical Atlantic arriving in the second half of July and the first half of July 23 are characterized by low ozone and CO, high RH as well as NO_y < 0.1 ppb (i.e., even slightly less than in the stratospheric air intrusion on July 22).

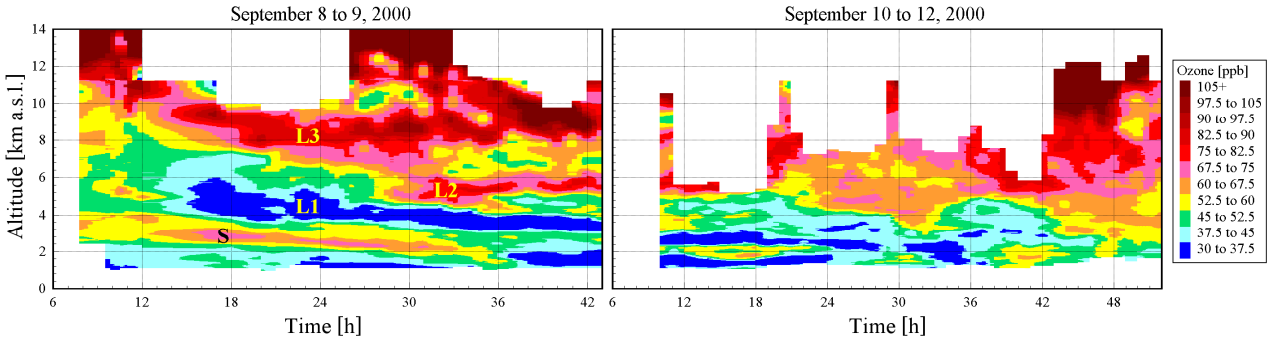

Fig. 4: Four-day lidar series September 8 to 12, 2000, starting during the early phase of a high-pressure period (full series: (Trickl et al., 2003), Fig. 13); S marks a stratospheric air intrusion, the layers marked with the labels L1 to L3 are discussed in the text. The time scale is given with respect to 0:00 CET on September 8. The gap during the night between September 9 and 10 is due to unauthorized closing the flap in the roof during the measurements.

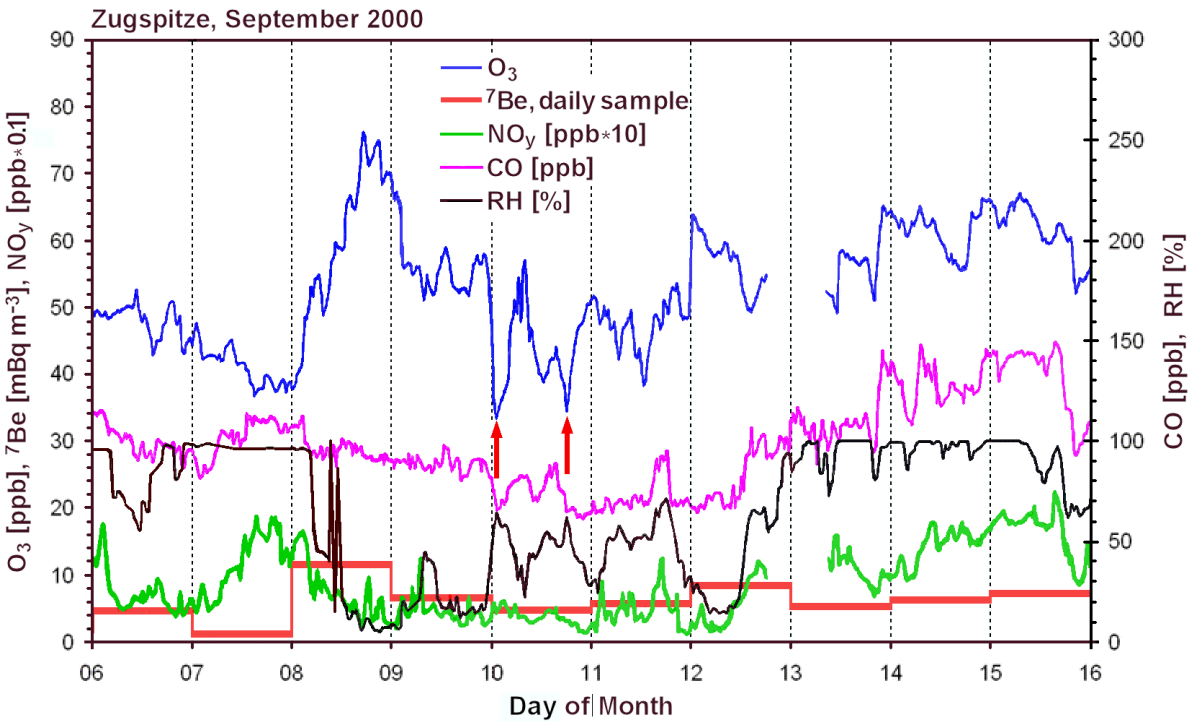

Fig. 5: Zugspitze summit, September 6 to 15, 2000 (CET): ozone, CO, RH and ^{7}Be; the red arrows mark the passage of the subtropical layer L1 (see Fig. 4) during the night hours of September 10, characterized by a decrease in O_3 and CO and an increase in RH. The NO_y mixing ratios at the times of the two ozone minima are slightly elevated with respect to the lowest values during that period.

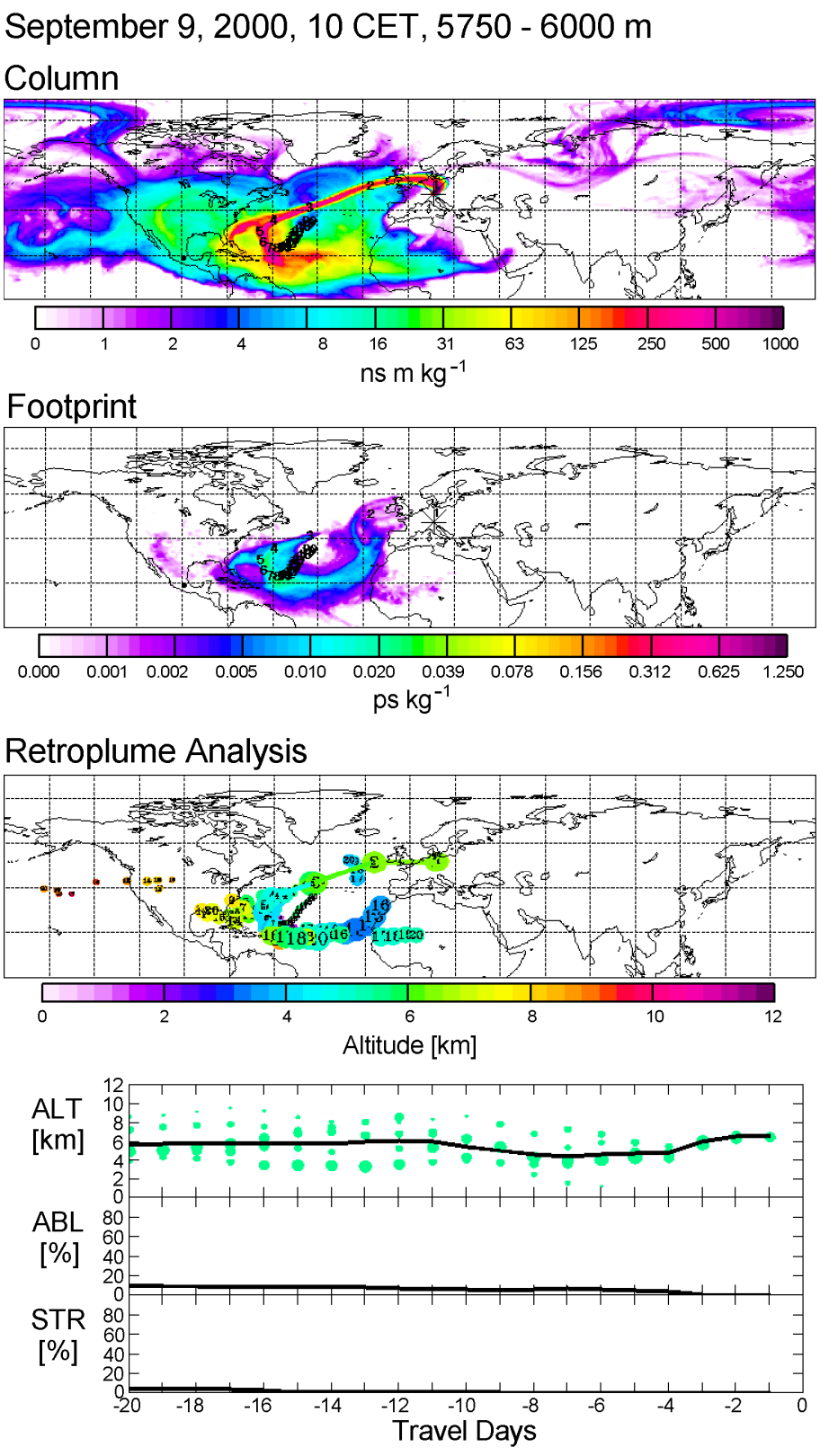

Fig. 6. 20-day backward simulations for September 9, 2000, 10 CET, initiated in the altitude range between 5750 and 6000 m: Tracer column, footprint and retroplume analysis; no clear reason for the elevated ozone values observed in this altitude range is visible.

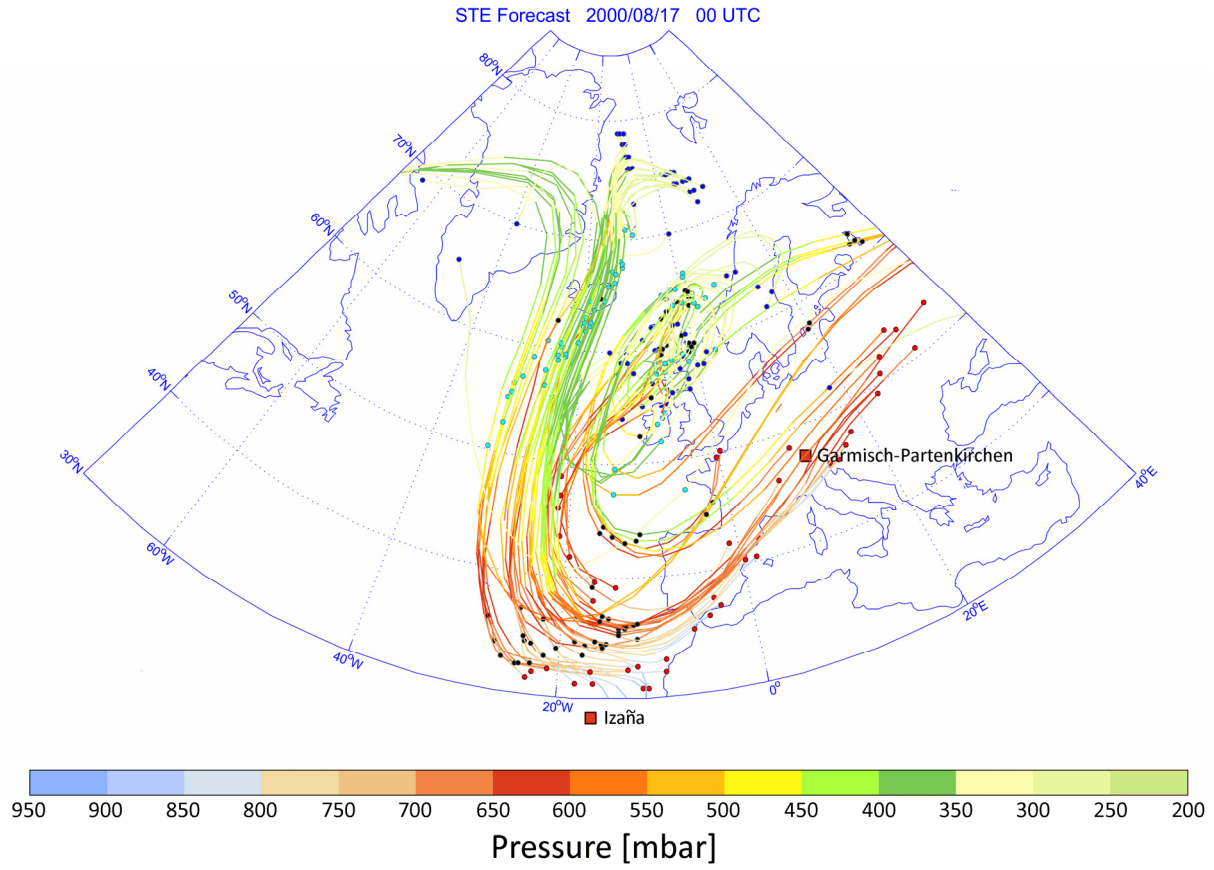

Fig. 7. LAGRANTO intrusion trajectories initiated on August 17, 2000, at 0:00 UTC (1:00 CET); the trajectories cover six days and are marked by symbols every two days, a blue dot for t = 0, a blue circle for t = 2 d, a black circle for t = 4 d, and a red circle for t = 6 d. The positions of Izaña (Tenerife) and Garmisch-Partenkirchen are marked by red squares.

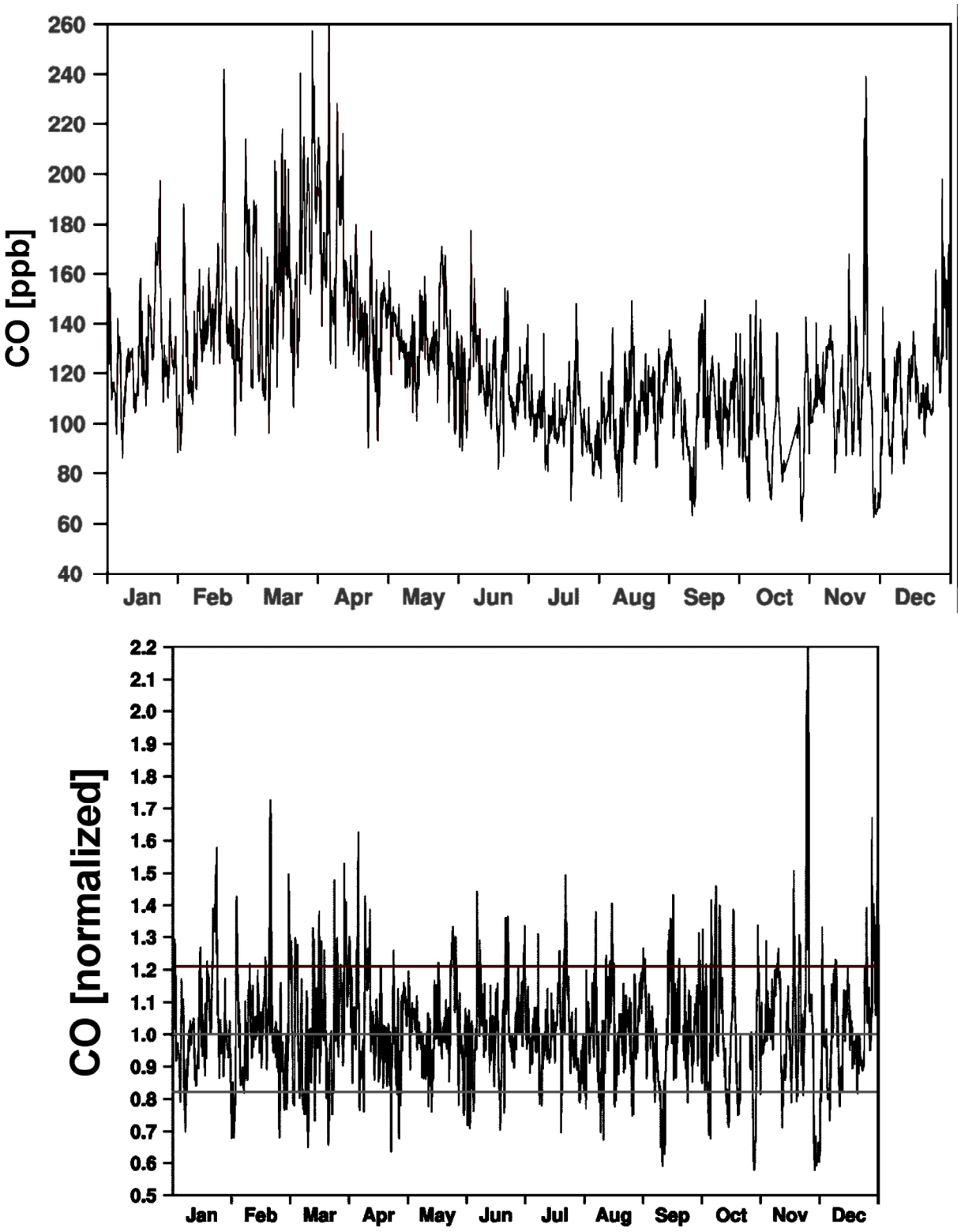

Fig. 8. Zugspitze CO for the year 2000; upper panel: three-hour averages formed from the measurements; lower panel: normalized with respect to a thirty-day moving average; the upper and lower horizontal line represents the 90^{th} and 10^{th} percentile, respectively.

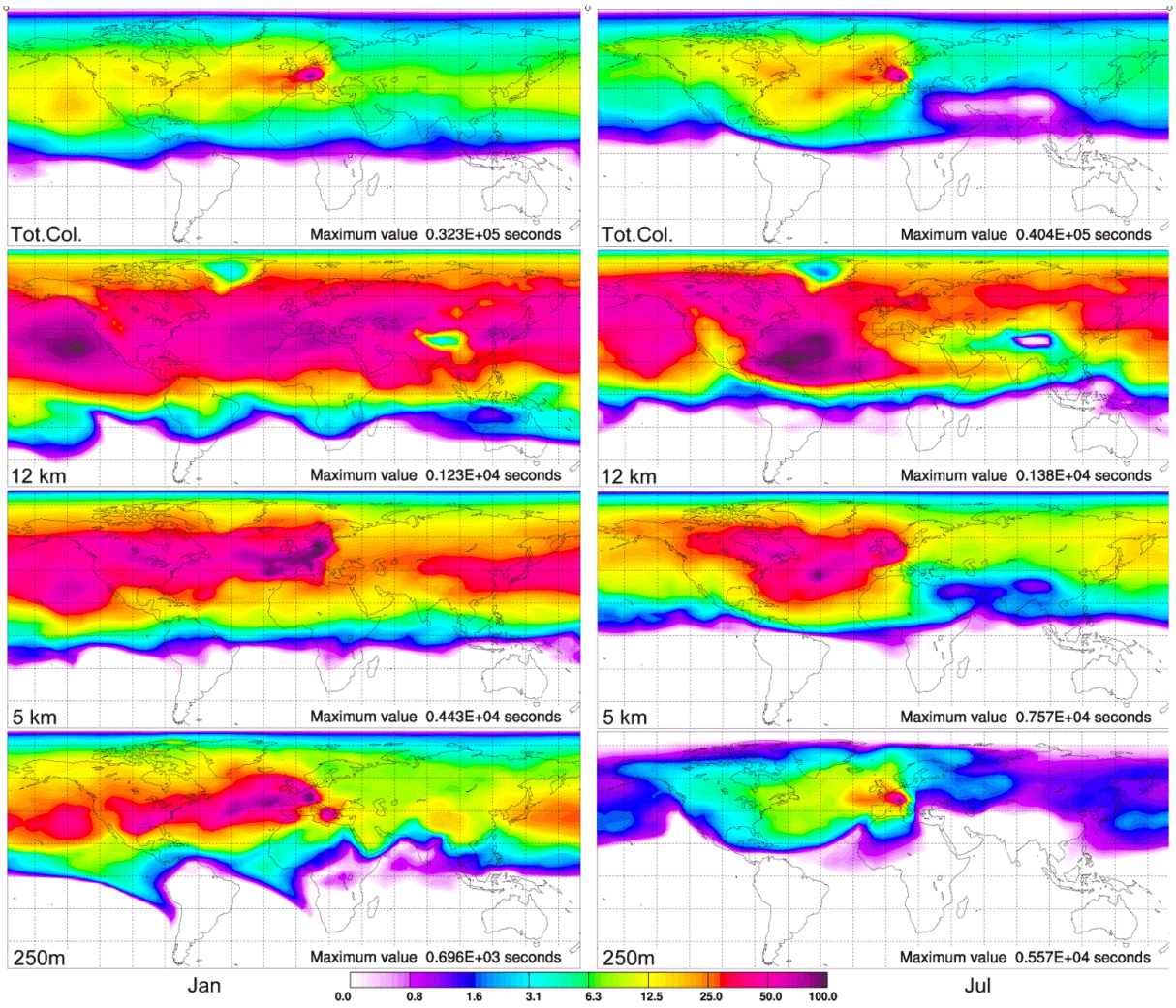

Fig. 9. Mean FLEXPART sensitivities for the fourty-day backward simulation integrated over the full atmospheric column, 12 km, lowest 5 km and lowest 250 m a.s.l.; the panels in the left column show the results for January 2000, those in the right column the results for July 2000. The colour scale is normalized to 100 %, the individual maximum values are given inside each panel.

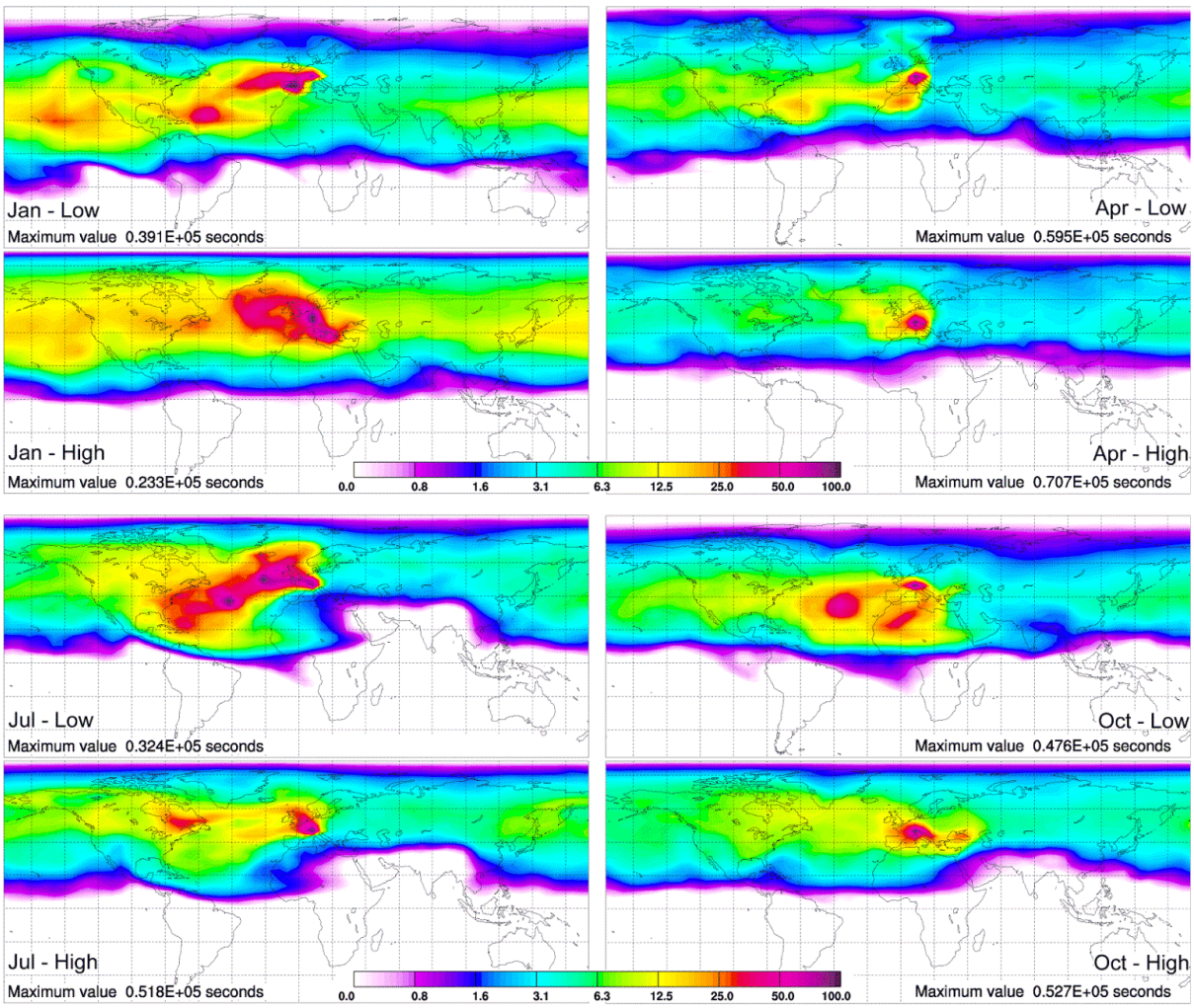

Fig. 10. Mean FLEXPART column-integrated emission sensitivities for the fourty-day backward simulation for release at the Zugspitze summit in January, April, July and October 2000. Only times were selected when the CO values were within the uppermost and lowermost 10 %.

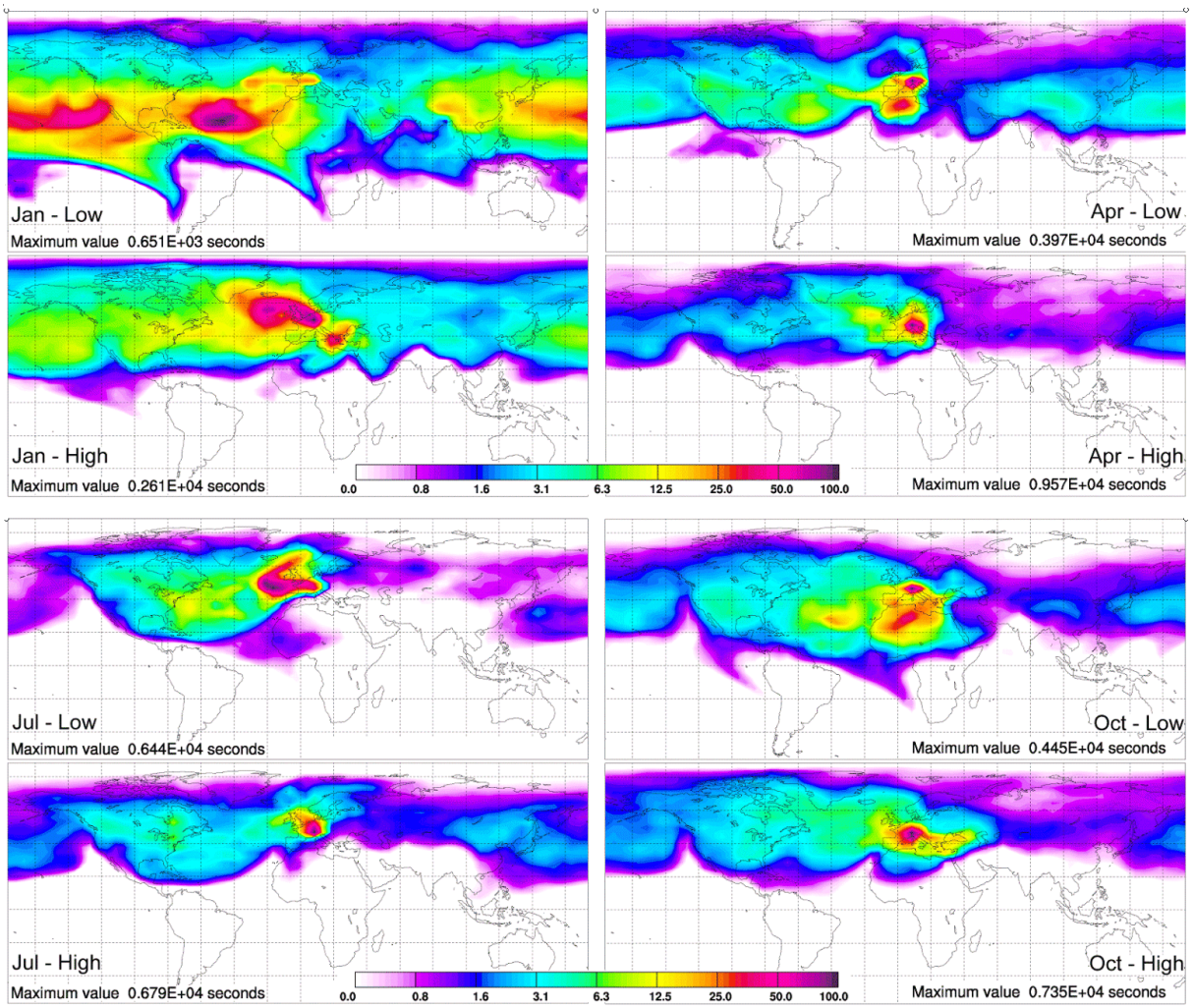

Fig. 11. Same as Fig. 9, but for 250 m

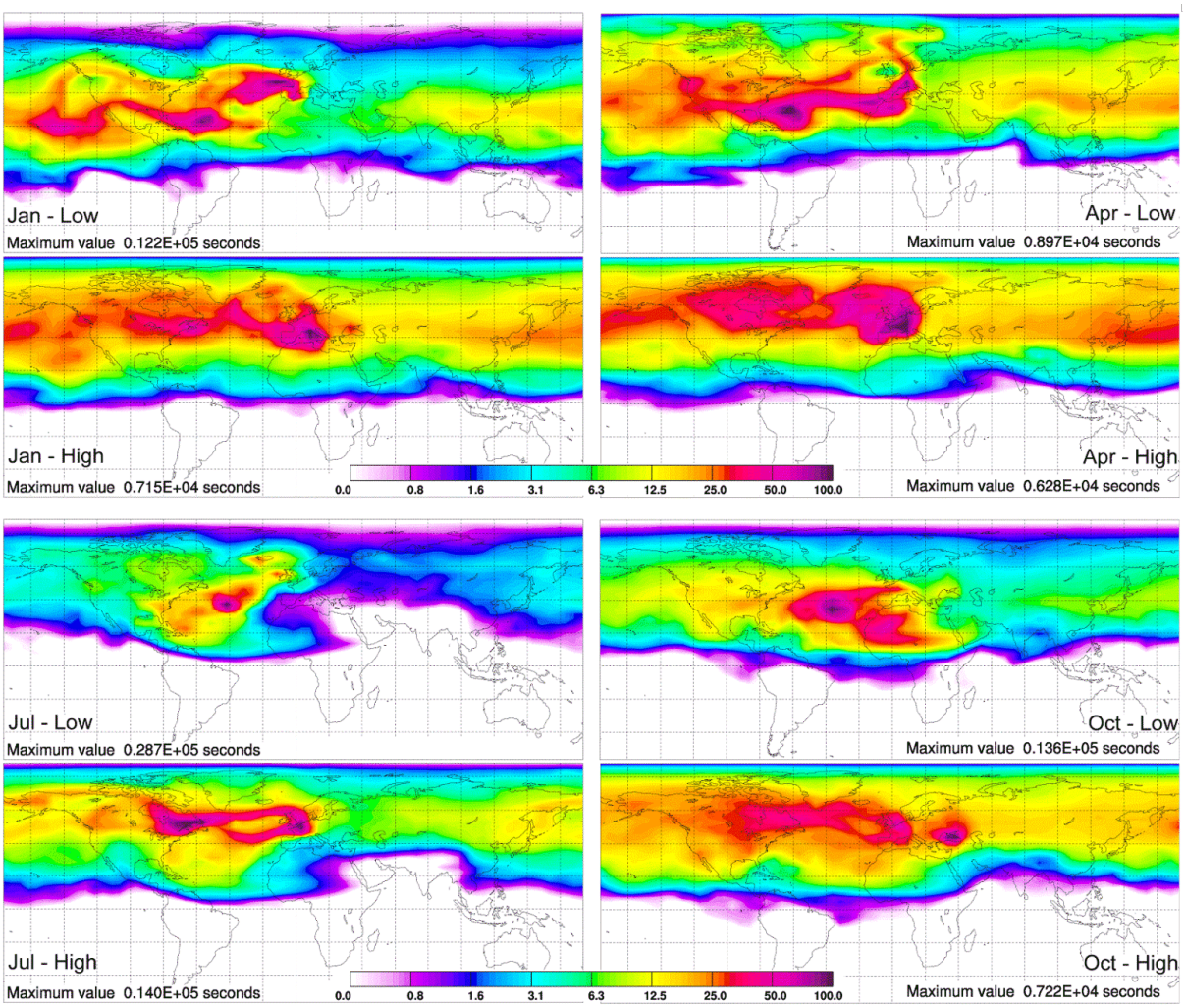

Fig. 12. Same as Fig. 9, but for 5 km

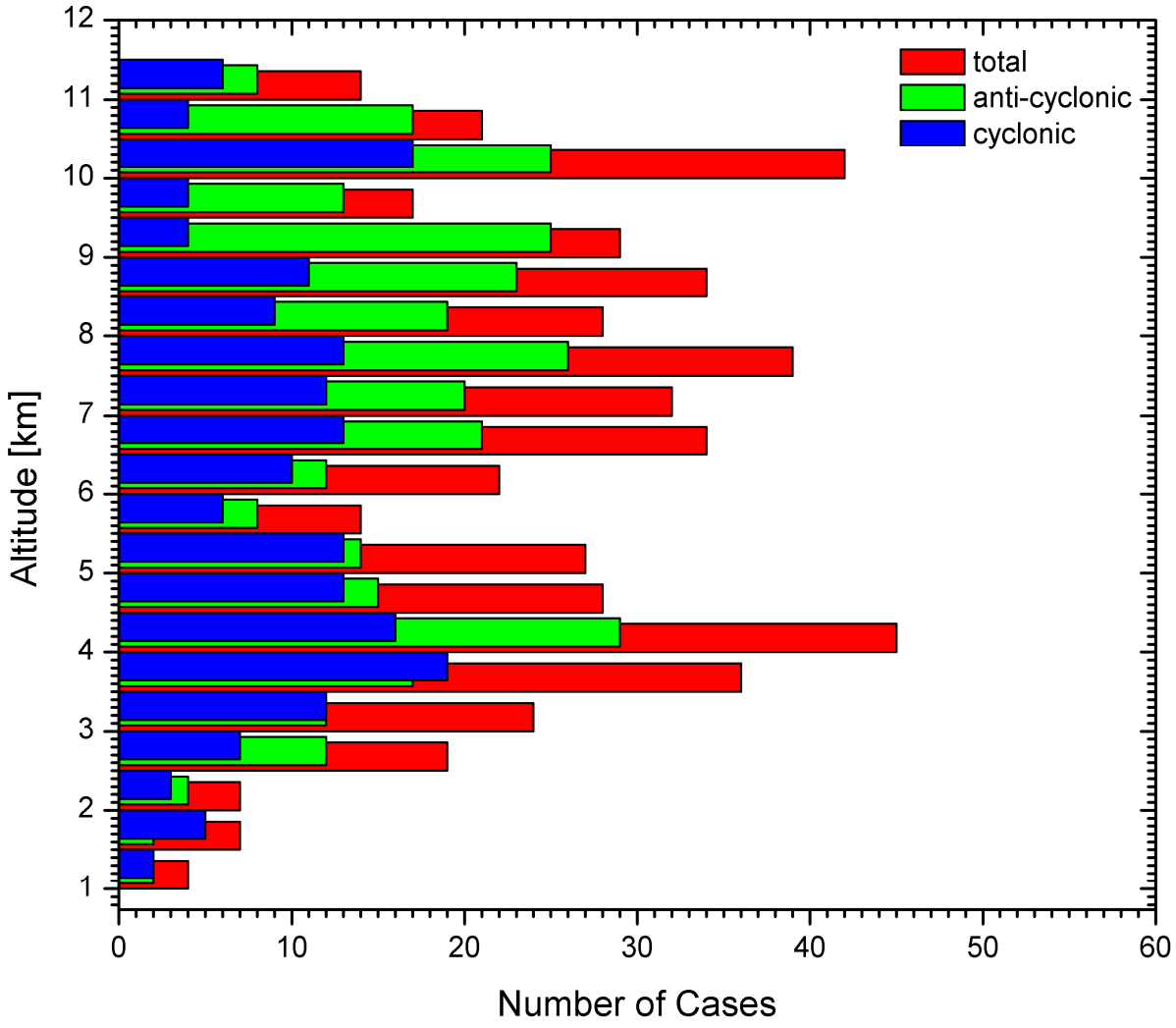

Fig. 13. Vertical distributions of the number of trajectory plots during the period April 2003 to September 2005 showing contact with the PBL over the subtropical Atlantic (see text); "anti-cyclonic" and "cyclonic" refer to the behaviour of the relevant trajectories prior to the air-mass arrival over Garmisch-Partenkirchen.

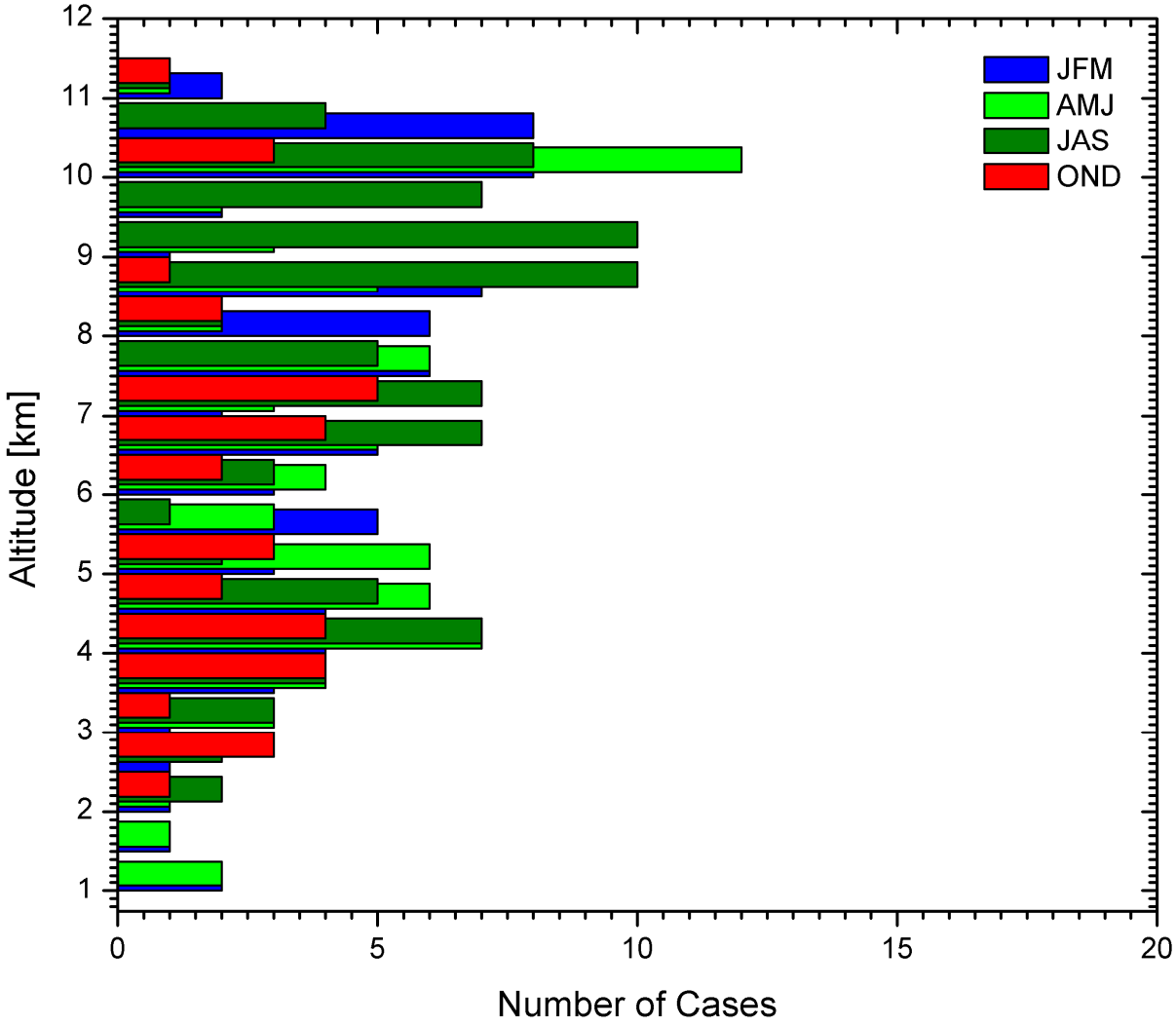

Fig. 14. Seasonal dependence of the vertical distributions of the number of trajectory plots during the period April 2003 to September 2005 showing contact with the PBL over the subtropical Atlantic for four different seasons (see text); JFM means "January to March", AMJ "April to June", JAS "July to September", and OND "October to December".