Atmos. Chem. Phys. Discuss., 9, 905–954, 2009
www.atmos-chem-phys-discuss.net/9/905/2009/

Atmospheric
Chemistry
and Physics
Discussions

This discussion paper is/has been under review for the journal *Atmospheric Chemistry and Physics (ACP)*. Please refer to the corresponding final paper in *ACP* if available.

Surface ozone at the Caucasian site Kislovodsk High Mountain Station and the Swiss Alpine site Jungfraujoch: data analysis and trends (1990–2006)

O. A. Tarasova[1,2], I. A. Senik[3], M. G. Sosonkin[4], J. Cui[5], J. Staehelin[5], and A. S. H. Prévôt[6]

[1]Max-Planck Institute for Chemistry, Mainz, Germany
[2]Moscow State University, Moscow, Russia
[3]Obukhov Institute of Atmosphere Physics RAS, Moscow, Russia
[4]International Center for Astronomical, Medical and Ecological Research NAS, Kiev, Ukraine
[5]Institute for Atmospheric and Climate Science, Swiss Federal Institute of Technology Zürich, Switzerland
[6]Paul Scherrer Institute, Villigen, Switzerland

Received: 15 October 2008 – Accepted: 19 November 2008 – Published: 13 January 2009

Correspondence to: O. A. Tarasova (tarasova@mpch-mainz.mpg.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Long-term ozone measurements of two background mountain sites, namely the Kislovodsk High Mountain Station in Caucasus, Russia (KHMS, 43.70° N, 42.70° E, 2070 m a.s.l.) and the Jungfraujoch in Switzerland (JFJ, 46.55° N, 7.98° E, 3580 m a.s.l.) are compared. Despite of more than 1.5 km altitude difference ozone concentrations are comparable at JFJ an KHMS in the beginning of measurements (1990–1993) while the annually averaged levels at JFJ are around 15 ppb higher than the ones at KHMS for the most recent years (1997–2006). Averaged for different periods ozone concentrations at KHMS are comparable with the respective values observed at the elevated sites in the midlatitudes, situated in the altitude range 1600–2400 m a.s.l. Distribution function of the hourly concentrations has two peaks at JFJ and it is close to Gaussian distribution in the case of KHMS. Seasonality at both sites is characterized by double spring-summer maximum. Spring maximum at both stations is more pronounced for the air masses with the longest contact with upper free troposphere and stratosphere. Average concentrations increased at JFJ but decreased at KHMS for the period 1990–2006. Trends are more pronounced for the 1990s (+0.73±0.20 ppb/year at JFJ and −0.91±0.17 ppb/year at KHMS for the period 1991–2001) in comparison with later years (+0.04±0.21 ppb/year at JFJ and −0.37±0.14 ppb/year at KHMS for the period 1997–2006). Trends show a distinct seasonality, which is different for the different periods. To investigate possible reasons for this remarkable trends difference 3-D trajectories using LAGRANTO trajectory model are used. Effects of the horizontal and vertical transport on ozone trends are considered. In general we could not find any systematic changes in the transport patterns which could explain the significant changes of the trends between 1991–2001 and 1997–2006. It is likely that the position of the main emission source areas relative to the stations is among the main reason for the opposite surface ozone trends. During the 1990s the JFJ trend reflects increase of the ozone in the upper free troposphere/lower stratosphere. In contrary KHSM is much more influenced by dramatic

emission decrease in the earlier 1990s in former USSR and emissions regulations in Western Europe. For later years ozone trends at KHMS are controlled by slight emission increase in the region, while trends at JFJ correspond to the scenario of European emissions control.

1 Introduction

Ozone plays a crucial role in tropospheric chemistry as it is the most important compound of photooxidant air pollution, it determines the oxidation capacity as the main precursor for OH radical and it is a significant greenhouse gas (IPCC, 2007). Surface ozone concentrations are very variable both in space and time, on both long and short scale. Trend determination of tropospheric/surface ozone is often a difficult task because the accuracy of the ozone gas analyzers is sometimes smaller than observed long-term changes (Virgazan, 2004; Oltmans et al., 2006; Brönnimann et al., 2002; TOR-2 report, 2003; Jaffe and Ray, 2007). Nevertheless it is well established that surface ozone concentration at unpolluted sites in Europe increased by more than a factor of two between the 1950s and the early 1990s (Staehelin et al., 1994), most probably because of large increase in ozone precursor emissions. Since the late 1980s measures are undertaken to reduce ozone precursor emissions in Western European countries. During the 1990s anthropogenic NO_x emissions deceased in Germany and Switzerland by more than 30%, the VOC decrease was even larger (EMEP, 2004). Problems of the former Soviet Union (USSR) in the beginning of the 1990s caused an economic crisis which led to a dramatic decrease of ozone precursors' emission in all countries of the former SU, and especially in the industrial centers.

Ozone concentration in ambient air does not show a simple linear response to the ozone precursor (nitrogen oxides (NO_x: $NO+NO_2$) and volatile organic compounds (VOCs)) emission changes. It has been shown, that peak ozone concentrations over Europe decreased (TOR-2, 2003; Jonson et al., 2006, and references therein) since the early 1990s, but the decrease in high ozone concentrations was rather small in the planetary boundary layer (PBL) of the Swiss plateau (Ordóñez et al., 2005). At the same time background ozone concentration over Europe substantially increased during the 1990s. Simmonds et al. (2004) showed that background ozone in the clean oceanic sector measured at Mace Head, Ireland increased by about 8 ppb for the period 1987–2003 (more in winter than in summer). Substantial increase of the surface ozone concentration was documented for European high alpine sites (Jungfraujoch, Zugspitze, Sonnblick) by Brönnimann et al. (2002) and Ordóñez et al. (2007). Thouret et al. (2006) and Zbinden et al. (2006) reported from regular aircraft measurements MOZAIC an overall increase in ozone concentration in the upper troposphere and the lower stratosphere of about 1%/y for 1994–2003 (extending over Europe, North Atlantic and Eastern US). Similar results were obtained during the GASP program (Schnadt Poberaj et al., 2007). Jaffe and Ray (2007) reported increasing ozone levels for most of the elevated locations in the Eastern rural USA regions for the 1990s.

Several reasons can cause long-term ozone changes at particular receptor site, including the response on the emission changes (both natural and anthropogenic), changes of the stratospheric contribution and changes of the transport patterns (both of horizontal and vertical direction). These processes can affect the trends differently in the individual seasons. An ozone precursor increase is expected 1) to increase ozone concentration by photochemical formation downwind of emission sources in the warm season, 2) to decrease ozone in winter due to growing effect of ozone titration by NO. Stratospheric ozone contribution is expected to be most important for spring trends due to stratospheric ozone maximum in this season, hence an increase of the stratospheric flux should provide strong positive trend in spring. Changes in the transport patterns can cause trends of both signs depending on the spatial ozone distribution and precursors' concentration changes in the areas of air masses origin.

Up to now the reasons of the background ozone growth in Europe are still under debate. Moreover, the observed trends are not reproduced by global models (Jonson et al., 2006; Stevenson et al., 2006). For example, Jonson et al. (2006) showed that decreasing European NO emissions can explain only part of the observed increase in winter ozone at polluted sites (due to decrease in titration) and the decrease in the high summer ozone episodes was less than expected. Therefore it was suggested that changes in ozone concentration advected to Europe could have partially compensated the expected decrease. This was corroborated by Andreani-Aksoyoglu et al. (2008) for model analysis of Swiss ozone trends. Among the reasons considered to explain positive ozone trend in the Northern Hemisphere the dramatic increase of South-East Asia emissions since 1990 was considered by several authors. Estimates obtained with state of art global numerical simulations (e.g. Auvray and Bey, 2005) can only partially explain ozone winter increase at high alpine sites. Ordóñez et al. (2007) suggested that an increased transport of ozone from the stratosphere could be responsible for a substantial part of the increase in the background ozone found at European mountain sites.

In this study we compare long-term ozone measurements at Kislovodsk High Mountain Station (2070 m a.s.l.) located at the Eastern border of Europe at Caucasus Mountains, and those of the mountainous site Jungfraujoch (3580 m a.s.l.) located in the Swiss Alps with the aim to understand the reason of the different ozone behavior at two background stations. Trajectory analysis is used as a tool to separate the air masses of different origin and to study the contribution of the different source regions to the observed variability of the surface ozone concentration at two mountain regions.

2 Measurements and methods

2.1 Ozone measurements

Continuous measurements of the surface ozone concentration used in this paper are performed at Kislovodsk High Mountain Station (KHMS) (43.70° N, 42.70° E, 2070 m a.s.l., Caucasus mountain region) and at Jungfraujoch station (JFJ) (46.55° N, 7.98° E, 3580 m a.s.l., the Alps). The map showing position of the sites is presented in Fig. 1. In the paper ozone concentration time series from 1990 to 2006 with hourly resolutions are used for both stations.

Kislovodsk High Mountain Station is situated on the mountain plateau 18 km to the south of the resort town Kislovodsk and 48 km to the north of the highest top of the Caucasus, Elbrus mount (5642 m). The site is situated on the plateau at the northern slope of the side Caucasus crest. The main Caucasus Ridge is located to the north of the site nearly along the latitude line (W-NW to E-SE), and it disturbs the main northern midlatitudes airflow (Westerlies) much less in comparison with the Alps in Europe. A more detailed station description can be found in Tarasova et al. (2003 and references therein) and Senik et al. (2005). The ozone instrument used at Kislovodsk (DASIBI model 1008-AH nr. 4565) is based on UV photometry and it is regularly calibrated. In earlier years the calibration was performed against transfer standard of Max-Planck Institute for Chemistry in Mainz (Germany) (DASIBI-1008RS nr. 6394). Since 2003 the calibrations are done directly and indirectly. The direct calibration is performed by a comparison with a secondary standard instrument (Env. O3-41M, nr. 1298) of the Obukhov Institute of Atmospheric Physics (Moscow, Russia) calibrated in Stockholm against primary standard SPR nr. 11. Indirect calibrations (pre-calibration) are carried out using the transfer standard DASIBI-1008RS nr. 6394 in accordance with a methodology described in Klausen et al. (2003) for the subsequent comparison of the working instrument DASIBI 1008-AH nr. 4565 (at KHMS) with the transfer (secondary) standard device Env O3-41M nr. 1298 (in Moscow). Calibrations are carried out in accordance with the international standard (ISO 13964). The accuracy is expected to be 1–2 ppb. Measurements at the station are continuously performed since 1989. The dataset has some gaps due to instrument transportation to calibration centers, instrument service or critical weather conditions (long dense fog).

Jungfraujoch is situated at the north-western slope of Swiss Alps (Fig. 1) and resides most of the time in the free troposphere, particularly in winter and often in spring and autumn (Zellweger et al., 2003; Henne et al., 2005). Detailed description of the site can be found in several publications (EMPA, 2000; Schuepbach et al., 2001; Zanis et al., 2007). O_3 concentration is continuously measured within the Swiss National

Air Pollution Monitoring Network (NABEL) using a commercially available instrument (Thermo Environmental Instruments, Model 49C, UV absorption). The instrument is regularly compared to a transfer standard (TEI 49C PS) which is traced back to a NIST standard reference photometer. The detection limit is 0.5 ppb, the measurement uncertainty is determined to be ±2% (1 sigma), neglecting the uncertainty of the absorption coefficient.

Statistical characteristics of the ozone datasets and distribution functions are based on the hourly mean data. All ozone subsets connected with trajectory analysis are 5 hourly averages calculated on the basis of hourly mean selected from 2 h before to 2 h after air arrival to the respective station. This procedure does not impact obtained estimates of trends and characteristics of the seasonal cycles, but improves the data statistics in the cases of the data gaps directly at the time of air masses arrival.

2.2 Backward trajectories

To attribute variability characteristics to the properties of the air masses we use 3-D trajectories calculated with a help of the trajectory tool LAGRANTO (Wernli and Davies, 1997). The trajectories are based on the three-dimensional wind fields of the recent 40-years reanalysis data set (ERA-40) of the European Centre for Medium Range Weather Forecast; for the period after ERA-40 (i.e. after August 2002) operational ECMWF analyses is used instead. Trajectories are calculated for 10 days back in time and have 6 h temporal resolution. The altitudes of the sites are taken into account by choosing the appropriate arrival level, i.e. 650 hPa for JFJ and 750 hPa for KHMS.

Trajectories are used to trace the origin of the air mass arriving to the station both in vertical and horizontal direction. For this aim the diagnostic parameters potential vorticity (PV), altitude along trajectory and PBL height from meteorological re-analysis data are used to discriminate different vertical source areas. Air parcels coordinates along the trajectories are used to study the horizontal transport patterns.

Several filters were applied to select the air masses being in the contact with the free troposphere and the stratosphere (in the text referred to as FT/ST cases), namely:

- the altitude along the trajectory at least once exceeds 400 hPa level;
- the altitude along the trajectory at least once exceeds 500 hPa level and PV value exceeds 1.3 PVU;
- the altitude along the trajectory at least once exceeds 500 hPa level and PV value exceeds 1.6 PVU;
- the altitude along the trajectory at least once exceeds 500 hPa level and PV value exceeds 2 PVU.

Note, that altitude and PV criteria should be fulfilled simultaneously at some point of trajectory. The trajectory is considered as belonging to the mentioned subset independently of the time when the criteria were satisfied. This makes the selected classes non-uniform. The use of PV value alone as an indicator of the free tropospheric/stratospheric air is not sufficient due to complex topography of the studied locations, which can create some local flows with higher PV.

Two filters are applied to trace the air masses which were in recent contact with continental PBL:

- the altitude along the trajectory is at least once lower than PBL height east of 10 W;
- the altitude of the trajectory is lower than PBL height at least during two days of the last 5 days before arrival to the site (without geographical limitation).

The trajectories filters are applied to the 5-hourly averaged ozone concentration at each site (see above). It should be noted that all the cases (FT and PBL) are studied independently, i.e. the cases filtered out with a stronger criteria are included in the cases selected based on the weaker but similar criteria. The monthly mean ozone concentrations are calculated for the individual subsets. The filtered monthly means are used for average seasonal cycles calculation and for trends analysis both for annual means and for different seasons. Because the concentration changes are not uniform in time we consider and compare two different time periods, namely 1991–2001 with large concentration changes at both site and 1997–2006 when ozone changes were much smaller.

To analyze the impact of the horizontal advection on the observed variations of the surface ozone concentration the trajectories arriving to the sites are classified. Cluster analysis is performed for the trajectories of the total length (10 days back) and for the whole period (1990–2006) so that the main transport directions are the same for the different considered periods (1991–2001 and 1997–2006). The classification is done by means of k-mean clustering of the horizontal air parcel coordinates (latitude and longitude) as the most impacting variables (the algorithm can be found for example in Cape et al., 2000, and in Tarasova et al., 2007, and references there in). Vertical transport occurs much slower which makes the vertical coordinate less variable and hence less efficient for trajectory's bunches discrimination. Similar number of clusters was selected for both sites (7).

One can argue that transport patterns may have changed from the period 1991–2001 to the period 1997–2006, so classification should have been performed for the selected periods separately. But selected procedure can take these changes into account by means of the interannually changing frequency, while classification of the separate periods makes it difficult to compare the obtained clusters.

3 Results

3.1 Concentration statistical characteristics and distribution functions

Figure 2 shows the monthly mean concentrations with standard deviation at JFJ and KHMS, calculated based on the hourly mean concentrations. In the beginning of the dataset (1990–1993) the measured concentrations at the two elevated sites are quite close to each other. In 1991 the lowest annual concentration is observed at JFJ for the whole 16-years period and in contrast the highest concentration is observed at KHMS. Since 1991 till 1996 a strong increase of the surface ozone concentration is observed at JFJ and strong decrease occurs the same time at KHMS, whereas in the later period ozone concentrations at both sites stabilized. The decrease at KHMS for the 90-s was first documented by Senik and Elansky (2001), while the most recent data were not published yet. Average rates of change for the whole period 1990–2006 are shown in Table 1 together with the other statistical characteristics of the datasets based on the hourly mean concentrations. Due to anomalous ozone variations in 2005 and 2006, statistics for these particular years is presented separately in the last two columns of the Table 1. Average ozone concentration exhibits pronounced vertical gradient in spite of rather high elevation of both sites. In Europe a distinct vertical gradient is mostly reported for the measurements up to 1200 m a.s.l. (Chevalier et al., 2007) while the picture is less consistent for more elevated sites (see Table 2).

Comparing the levels of the surface ozone concentration at KHMS with literature data we can see (Table 2), that average concentration at KHMS (2070 m a.s.l.) for the period 2001–2004 is close to the observations at Arosa (1840 m a.s.l.). Le Casset (1750 m a.s.l.), another station, which is even lower than KHMS, has slightly higher average concentration but still in the limits of 1 standard deviation of the average concentration estimate (Chevalier et al., 2007). Comparing KHMS ozone levels with the data reported for USA sites by Jaffe and Ray (2007) we can find comparable concentrations (see Table 2) at Craters of the Moon, ID (1815 m a.s.l.) and Yellowstone N.P., WY (2400 m a.s.l.). Hence, the average ozone concentration observed at Caucasus region is consistent with the other observations at the elevated sites of the northern mid-latitude (in the altitude range 1600–2400 m a.s.l.). At the same time among the reported sites at the levels 1600–2800 m a.s.l. quite substantial variability of the average ozone concentration is observed, which may be connected with different pollution level at the sites and different impact of complex orography. Nevertheless approaching to 3000 m a.s.l. average ozone concentration usually exceeds 50 ppb. Among the less elevated stations the average concentration higher than 50 ppb is only reported for

Monte Cimone, which is strongly affected by ozone and precursors advection from the heavily polluted Po basin (Campana et al., 2005; Cristofanelli et al, 2007).

The variance of the hourly concentrations is bigger at JFJ in comparison with the Caucasian station (Table 1) both for the whole data series and for 2005–2006 subset. Minimum hourly mean concentrations are comparable for JFJ and KHMS for the whole series, while in 2005–2006 ozone minimum concentration at JFJ is higher than at KHMS. This may be related with strong positive trend of the surface ozone concentration at JFJ, which is more pronounced for minimum values (Brönnimann et al., 2002).

The frequency distribution of the hourly mean values is close to Gaussian probability function for KHMS (see skewness of the distribution function in Table 1, and Fig. 3). Distribution of the hourly mean concentrations is asymmetric for JFJ and can be approximated by a superposition of two Gaussian functions (characteristics of the distribution are given in Fig. 3). Despite of the proximity of the KHMS' distribution function to the Gaussian shape, there are still some signs of the secondary peak formation which looks like a "shoulder" in the range of bigger concentrations (Fig. 3). The presence of two maxima in the distribution function can indicate the existence of the two typical regimes of ozone concentration. Double peak ozone distribution function is also reported for Mt. Cimone and Mt. Waliguan (Lee et al., 2007; Wang et al., 2006) with the first peak centers at 43 ppb and 45 ppb correspondingly. These values are in agreement with the main peaks of the ozone distribution at considered sites (45.5 ppb at JFJ and 43.4 ppb at KHMS).

3.2 Seasonal variations

The seasonal cycles at the KHMS and JFJ sites show higher ozone values in the warm season (for both locations two maxima are pronounced) and lower values in the cold season as typically observed at rural, remote and elevated sites in northern mid-latitudes (Tarasova et al., 2007), except the remarkably low values reported at KHMS in September and October in 1996 (Fig. 2a). Spring and summer maxima in the seasonal cycle are more distinguishable for KHMS than for JFJ. The highest ozone concentrations in the Caucasus and the Alps occur between March and August, depending on the particular year (Fig. 4). This is also the time period when mountain venting occurs transporting air from lower altitudes by convection to high altitudes (Henne et al., 2004; 2005). High ozone values observed in the summer 2003 at JFJ are connected to the very high temperatures of mentioned summer, which seem not only have affected ozone in the European Planetary Boundary layer (e.g. Ordóñez et al., 2005) but also ozone concentrations at JFJ. Record low ozone values were found at KHMS in September/October 1996 (the low values were confirmed by two instruments operated simultaneously) and the highest concentrations were registered in summer at JFJ in 2006.

A rather extreme amplitude of the seasonal cycle is observed at KHMS in 1996 and 2003 (27.7 ppb and 20 ppb). If not considering these outlying years the average amplitude of the seasonal cycle at Caucasian station has a tendency to decrease from 18.3 ppb in 1990–1992 to 12.8 ppb in 1997–2001 (Fig. 3). This change in seasonal variation amplitude is related to a strong decrease in spring/summer values whereas the decrease in ozone concentrations in the cold season is much smaller (Senik and Elansky, 2001; Tarasova et al., 2003).

Seasonal cycle of the surface ozone concentration at JFJ is also characterized by spring-summer maximum. The amplitude of the seasonal variations (difference between annual maximum and annual minimum) at JFJ has a substantial interannual variability, being extremely high in 1990 (29.7 ppb), 1994 (26.4 ppb), 2003 (24.3 ppb) and 2006 (23.9 ppb). The average amplitude of the seasonal variations changed from 22 ppb in 1990–1992 to 20.1 ppb in 1997–2001. But this change in the amplitude of the seasonal cycle can not be considered as significant due to its strong inter-annual variability.

The origin of the spring and summer ozone maxima at rural and remote sites has been discussed since many years. Historical records show spring maxima in earlier years (Linvill et al., 1980; Monks, 2000; Nolle et al., 2005), although the shape of the cycle is likely to be sensitive to pollution conditions (see e.g. Scheel et al., 2003). In the earlier time surface ozone maximum was typically found in May (e.g. at Arosa) and it was attributed to the mixing with stratospheric air (e.g. Götz and Volz, 1951; Staehelin et al., 1994). Surface measurements and ozone sounding at rural and semi-polluted sites in north America and Europe from the 1980s (Logan, 1985) and the 1990s (Tarasova et al., 2007, and references therein) often show a shift of the seasonal maximum to summer, which is commonly attributed to photochemical ozone production related to anthropogenic emissions of ozone precursors.

While analyzing the variability and the formation of the seasonal cycle it is important to consider which role is played by air transport in the mentioned processes. Figure 5 shows the results of backward trajectory analyses attempting to discriminate between the effect of mixing with stratospheric air and recent contact with the (polluted) planetary boundary layer. Air parcels defined as "UTLS" (i.e. PV values larger than 2 PVU and altitude higher than 500 hPa at least once along the trajectory) show a general tendency to have higher ozone concentrations than the averages, while the air parcels defined as having contact with PBL (at least 2 days of the last 5 before arrival at the station the air parcel was inside PBL, which altitude is retrieved from reanalysis data along trajectory) have ozone concentration a bit lower than average, except for July. The only slight enhancement in the UTLS class as compared to the mean monthly concentrations suggests strong mixing with tropospheric air prior to the arrival to measuring site. It is also interesting to note that the strongest enhancement for the "UTLS" subset at both sites is observed in May, when ozone concentration is the highest in the lower-most stratosphere in the northern extratropics. Monthly mean concentrations in the PBL subsets are a bit lower than average during the cold season which probably reflects the effect of ozone poor PBL air (e.g. caused by ozone dry deposition and titration with NO).

The major transport ways to each station are presented in Fig. 6. As it can be seen for both locations Western clusters are prevailing. At the same time even Western clusters are affected by the different areas of impact, i.e. the sampling is more often

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀▌ ▐▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

over the Atlantic Ocean for JFJ and over different European regions for KHMS. It should be noted that the clusters representing the transport of the longest range are observed in total in less than 5% of cases for both locations. Substantial number of cases (around 18% at JFJ and 22% at KHMS) corresponds to the transport on the regional/local scale.

Average seasonal cycles are calculated for the different clusters of the horizontal advection (Fig. 7). Two important features can be seen in the graphs, which are similar for both sites (JFJ and KHMS). The highest spring maximum is observed in May in the cluster, originating in the East Asia (cluster 1 for KHMS and cluster 5 for JFJ). For the other clusters representing long-range transport and traveling in the upper part of the troposphere the seasonal variations are the same, i.e. with prevailing spring maximum (clusters 5 and 3 for JFJ and cluster 6 for KHMS). Statistical significance of the relative contribution of the mentioned clusters to the average seasonal cycle is not very high due to low frequency (less than 3%).

Second important feature, which is the same for both locations, is the excess of the summer maximum above the spring one in the cluster of the local/regional transport (cluster 4 for JFJ and cluster 3 for KHMS). These clusters for both stations have the highest frequency of the contact with the polluted continental PBL and are associated with a very slow transport (stagnation condition). Summer maximum which is developed in local clusters is associated with ozone photochemical production in the polluted air, hence indicating the connection of the summer maximum with photochemical processes. Slight excess of the summer maximum above the spring one is observed in the other clusters, which spent long time over the continent (for example, in cluster 7 for JFJ). For the clusters impacted by the European PBL arriving at KHMS spring and summer maxima are of comparable magnitude.

3.3 Trend analysis

As it has been mentioned above, long-term trends of the surface ozone concentration have different tendency, which value also depends on season (Fig. 8). In the following chapter the trends of the surface ozone concentration are analyzed at Kislovodsk

(Sect. 3.3.1) and at Jungfraujoch (Sect. 3.3.2) making use of the data obtained by backward trajectory analysis. The trends are calculated for different time periods (1991–2001 and 1997–2006) and transport subsets. Vertical subsets are discussed first so that the main finding can be used in the interpretation of the trends in the clusters of the horizontal advection. Analysis of the frequencies of the cases for each particular subset did not reveal consistent long-term changes to explain the systematic ozone trends (Fig. 9b, d), while the variability of the shorter scale (inter-annual) correlates to a certain degree with the variability of the transport patters. Working on the trends explanation we also considered the impacts of the changes of tropopause height and geopotential height at 500 hPa to understand the role of the dynamical processes better. We found that the trends of the mentioned parameters have different signs at KHMS and JFJ, showing the difference in regional dynamics. But to the moment we can not draw a conclusion on the role of these factors in resulting trends formation.

3.3.1 Trend analysis for ozone measurements at Kislovodsk High Mountain Station

Ozone trends at KHMS separated by the vertical transport classes (including planetary boundary layer contact and stratospheric origin, see Table 3 and Fig. 9a) are negative and statistically significant in 1991–2001 for all selected classes. Difference between trends in FT and PBL classes is insignificant. Maximum negative trends at KHMS (Table 3) are observed in summer and minimum negative trends are observed in winter (FT cases) or in autumn (PBL cases). Such trends seasonality (most negative in summer and the least negative is winter) can be explained by ozone precursors emissions reduction which occurred in 1990s in Europe due to implied regulations and in the Newly Independent States due to USSR breakdown accompanied by economical crisis. KHMS is situated further deep in the continent which provide higher probability of the arriving air masses to contact planetary boundary layer anywhere over the continent and bear the signs of emissions decrease both in Europe and more local regions. The area from which the air is sampled in the subset of the strongest PBL criteria (2 days of the last 5 before arrival to the station should be spent in the PBL) covers mostly the Northern Caucasus region (not shown here). The trends in the FT subsets at KHMS are also negative despite of the reported increase in the 1990s of the stratospheric ozone contribution in the troposphere (Ordóñez et al., 2007). Among the reasons to explain at least the part of this bias to the negative values the following could be mentioned: 1) quite substantial impact of the PBL on the ozone levels at KHMS (especially in summer with developed convection over the continent, hiding the effects of ozone increase at the higher levels in the troposphere); 2) poor description of the mixing processes in the trajectory model which leads to misinterpreting the FT cases; 3) geographically different FT sampling area in comparison with JFJ (the picture is not shown). Nevertheless, the selected approach should be considered as a compromise, which let us see the signs of the stratospheric air in the admixture measured at the site. One more point is that for KHMS total time of the contact with the upper troposphere/lower stratosphere (PV>2 PVU and $p<500$ hPa) in comparison with JFJ in 1991–2001 is much smaller (31578 total hours against 64038 h at JFJ), so the effect of the ozone concentration growth in the free troposphere over Atlantic is less important for KHMS.

Ozone trends in the different vertical subsets are much smaller at KHMS in 1997–2006 in comparison with the earlier period (Table 4, Fig. 9a), being in the range from -0.3 to -0.6 ppb/year. Pronounced trend differentiation is observed between the average PBL (more negative) and FT trends. But this difference can be opposite for the seasonal trends (winter and spring trends in FT cases are more negative than the PBL cases). The number of cases of the air contact with PBL at KHMS has increased in 1997–2006 in comparison with the period 1991–2006 (from an annual average of 15.8% to 18.4%) showing the increase of the PBL impact on the trends formation at KHMS.

Figure 9a shows that seasonality of the trend at KHMS for the period 1997–2006 differs from the one during earlier years (compare also Tables 3 and 4). Summer trends from the most negative became the closest to 0, which can indicate the transformation from the decreased ozone summer production to the stabilization of summer production or even its increase (note, emissions of the former Soviet Union did not decrease further or started increasing again since 1997–1998 due to economics stabilization). Moreover the most significant changes of the seasonal trends occurred in particular during summer (from the range −1.2…−0.9 ppb/year in 1991–2001, to the range −0.24…+0.12 ppb/year in 1997–2006). Winter trends in the strictest PBL subset (the lowest rows in Tables 3 and 4) have the same tendency and changed from −0.67 ppb/year in 1991–2001 to the least negative among all subsets in 1997–2007 (−0.08 ppb/year). Ratio of the summer and winter trends at KHMS during 1997–2006 more corresponds to the scenario of emissions increase (more negative trend in winter and less negative and even positive trend in summer). Ozone trends in the strictest FT subsets (PV>2 PVU) remain negative in 1997–2006 in spite of the general decrease of the total time, which trajectories spent in the region falling under the mentioned criterion (31578 h in 1991–2001 against 22980 h in 1997–2006).

Summary of ozone trends in the clusters of horizontal advection is provided in Tables 5 and 6. For the period 1991–2001 surface ozone trends at KHMS in all clusters and for all seasons are negative and statistically significant (Table 5) with somewhat wider range than in the vertical subsets. This means that the air masses can be better segregated accordingly to the geographical origin. Annual trends are in the range from −1.09 to −0.7 ppb/year. On average the most negative trend is observed (among the most contributing clusters) in the cluster 4, covering the Southern and Central Europe and originating over Central Atlantic. This may be connected with ozone decrease downwind of the area (Central and Southern Europe) with strong emissions regulations of ozone precursors. Similar negative trends are found in cluster 5 (−0.89 ppb/year), which originates over Central Europe, confirming the idea that negative trends at KHMS may be connected not only with local emissions decrease (see below) but also can be impacted by the air advection from Europe. In total clusters 4 and 5 constitute 55% of the air masses arriving to the station per annum. In summer cluster 3 representing local transport is the most frequent one (accounting for 44% of transport). North Caucasian region was well known as one of the oldest oil producing region in Russia (refinery region). For the period from 1990 till 1995 oil production in the region decreased nearly 3 times (from around 9 million tons to 3.78 million tons as reported by the State Committee on Statistics “Goskomstat” (1999) which means the decrease of accompanying emissions. Weather this decrease was sharp or gradual is unknown due to absence of statistical information. Therefore high ozone concentrations at the KHMS station were caused by ozone production in the air advected from PBL polluted by oil industry (see seasonal cycle in the corresponding cluster).

The difference between trends in different advection clusters at KHMS is larger if considering the individual seasons (Table 5). The largest trends scatter is observed in summer (from −1.43 to −0.67 ppb/year), while winter trends are much closer to each other (from −0.78 to −0.42 ppb/year). In general in most of clusters (except cluster 2) maximum negative trends are observed in summer, while the minimum negative trends are observed in winter/autumn. In summer cluster 3 is the most frequent one and ozone trends in this cluster are attributable to the decrease of ozone precursor’s emissions of the local scale. Moreover maximum impact of the PBL as shown above is expected in this cluster. Summer trends in the clusters 5 and cluster 4 might be impacted by Southern and Western European emissions decrease due to legislation. The trend of the surface ozone due to emissions regulation (at least of nearby emissions) should be positive in winter, while at KHMS all the trends are negative which may be attributed to the underestimated mixing in the trajectory model or with particular winter chemistry at the low ozone precursors levels. Interesting to note, that the bigger area is covered by a cluster, the stronger is the negative trend for both winter and summer (in winter −0.78 ppb/year for cluster 4, −0.62 ppb/year for cluster 5 and −0.42 ppb/year for cluster 3; in summer −1.43 ppb/year, −1.29 ppb/year and −1.04 ppb/year for the corresponding clusters), while the difference between summer and winter trends is similar for considered clusters. Smaller winter ozone trend in the cluster of the local advection may indicate either much higher rate of the local emission reduction in comparison with European regulations or different structure of the emission reduction (mostly industrial, oil-gas associated).

Unlike the discussed above clusters of the air advection to KHMS in 1991–2001, cluster 7 (originating at the West coast of US) has different properties. In this cluster the most negative trend is observed in autumn (–1.23 ppb/year) and the least negative trend is observed in winter (–0.62 ppb/year). The reasons for such a seasonal pattern of the trend are unclear. Relative contribution of the air arriving in this cluster accounts on average for less than 15%. It is likely that several processes contribute simultaneously into formation of the trend in the cluster 7.

Comparing the trends of the surface ozone concentration at KHMS for the period 1997–2006 (Table 6) with the earlier period, discussed above, we can see substantial decrease of the trends absolute values. For most of the clusters (clusters 2, 3, 4, 5 and 7) trends remain negative and statistically significant. The least negative trend is observed in the cluster 4 (originating in Central Atlantic), up to –0.18 ppb/year. Moreover, the most substantial changes of the trends' values and their seasonality are observed in this cluster (cluster 4). Taking into consideration that ozone source areas for KHMS are situated much lower than for JFJ, the shape of the trends seasonality (slight negative trend in winter and slight positive trend in summer might be the signs of the increased ozone production in the PBL over the Atlantic due to ship emission increase. In 1997–2006 spring trends became mostly statistically insignificant (with the exception of the cluster 7, for which it became just a bit less negative in comparison with the one for the period 1991–2001, i.e. changed from –0.75 ppb/year to –0.57 ppb/year). Proximity to 0 of the summer trends in the main advection clusters, i.e. cluster 3 (local), cluster 5 (Central Europe) and cluster 4 (Central Atlantic) and weak but statistically significant negative trends in winter in the considered clusters probably indicated the growth of the emissions to the South and West of the KHMS location, transported then to the KHMS and impacting ozone concentration levels.

3.3.2 Trend analysis for ozone measurements at Jungfraujoch

General features of the long-term ozone concentration evolution at JFJ for different seasons are presented in Fig. 8c. Summary of the trends in different vertical subsets at

JFJ is given in Tables 7 and 8 for the periods 1991–2001 and 1997–2006, respectively.

Table 7 shows that for the period 1991–2001 the trends at JFJ are positive and statistically significant for all the subsets (including seasonal). The value of the annual trends at JFJ ranges from +0.82 to +0.59 ppb/year (first column of Table 7). Trends are very close in all FT cases while they are smaller for PBL cases (especially for the air which was in the contact with PBL at least 2 days of the last 5 before arriving to the station). As far as we do not set a spatial criterion to the area of the sampling in the case of the last mentioned subset, the PBL may also b sampled over Atlantic.

All the trends at JFJ during 1991–2001 (Table 7) have pronounced seasonality, characterized by the most positive trends in spring and the least positive trends in summer and autumn. An exception is the subset with the longest contact with PBL, for which the strongest positive trend is observed in winter and the least positive trend is observed in summer. Ozone increase in winter is consistent with the ozone response to NO emissions reduction as expected from air pollutants abatement regulation (less titration of ozone in winter and less production in summer). However, the increase of the surface ozone concentration in the warm season contradicts to emission regulation strategy, which took place during the early 1990s. One may need to take into account that the PBL contact cases happen over large geographical regions, which are not uniform in the sense of emissions. PBL contact may occur both over the polluted Northern part of Italy and Spain, which probably impacts the most ozone concentration at the station and over the large parts of the North Atlantic, which is less polluted than continental Europe.

Seasonality of the trends in the FT cases (Table 7) can provide some more insight into the reasons of trends: 1) the trends are more positive in the FT/ST group indicating that at the higher levels in the troposphere the growth is more substantial. Ozone growth in the upper troposphere is connected with increased transport from the stratosphere (see Ordóñez et al., 2007); 2) as far as stratospheric ozone has seasonal maximum in spring the strongest response on the increased influx should be expected for the spring months, which is consistent with our analysis (i.e. the most positive trends in

FT subsets are observed in spring). The geographical area, where the stratospheric air is sampled before arrival to JFJ (not shown here) suggests that the UTLS regions over North Atlantic/USA East coast and Canada provide the strongest impact on the monthly means in the FT subsets. Therefore we can conclude that for the period 1991–2001 the trends at JFJ may mainly be caused by two factors, namely in situ emissions regulations, causing ozone decrease in summer and increase in winter in PBL overlapping with systematic increase due to the growth of the stratospheric contribution (mostly seen in spring). This conclusion is in line with the finding of Ordóñez et al. (2007) who provided evidence that ozone concentration at JFJ has increased in the 1990s in the free troposphere over Atlantic due to increased contribution of the stratospheric ozone.

The trends values are substantially different at JFJ for the later period, i.e. 1997–2006. On average the trends at JFJ (see Table 8, Fig. 9c) are statistically non-significant and close to zero (from +0.18 to –0.01 ppb/year). Change of the absolute values of the trends is accompanied by the change in the trends seasonality. The trends remain mostly positive and statistically significant is winter, unlike the other seasons. The only FT subset where trend remains positive and statistically significant in summer corresponds to the cases with "$p<400$ hPa", i.e. for the air which travels quite high but not necessarily had contact with the stratosphere. The cases which fulfill this criterion may correspond to the long-range transport of precursors and ozone from Asia. Note, that for the earlier period (Table 7) positive trend at JFJ was also the highest in summer for the mentioned FT subset. The least changes of the trends without changes of their seasonality between 1991–2001 and 1997–2006 are observed at JFJ in the subset with the longest contact with PBL (the lowest row in Table 8), hence ozone response to the emissions control over Europe is consistent for the two periods. The trends in PBL may be slightly weaker due to the fact that the rate of emission changes has decreased in 1997–2006 in comparison with 1991–2001. Indeed, according to the emission inventories presented by the EMEP program (http://www.emep.int) the rate of the EU15 (excluding Greece) emission decrease rate as reported by Parties declined from 1970 Tg/y to 1584 Tg/y for CO, from 326.3 Tg/y to 252.9 Tg/y for NO_x, from

507.6 Tg/y to 391.2 Tg/y for NMVOC during 1991–2001 and 1997–2006, respectively.

The strongest change in the magnitude of the spring trends is observed for the strictest FT subset, which may indicate that contribution from the stratosphere is not changing anymore and that the average trend is driven by emission regulations mostly. Absence of the positive trends during the warm season in 1997–2006 indicate that the earlier trends are likely to be only slightly driven by the increased ozone production over Eastern Asia, because emissions in the region were and are rising very fast (see for example van der A et al., 2008). As the response to the increasing emissions ozone production should continue rising while this is not clearly seen in the data.

The number of FT or PBL cases at JFJ has not changed much (Fig. 9d) which could have been important for the overall average trend as well. But the total time spent in the contact with the lowermost stratosphere (PV>2 PVU and pressure less than 500 hPa) has substantially decreased in 1997–2006 in comparison with 1991–2001. It reached 64038 h for the earlier period and only 52146 h for the later one. This difference by itself is not enough to explain the dramatic change of the trends at JFJ without assuming substantial changes in the source area.

Surface ozone trends at JFJ in the different advection clusters are summarized in Tables 9 and 10. As we have seen in the discussion of the vertical subsets, ozone trends at JFJ are positive and statistically significant for the period 1991–2001 in all advection clusters (Table 9). The most positive annual trends are observed in the clusters 1, 3 (both observed very seldom) and 6 (observed on average in 16% of cases), i.e. in the “longest” clusters traveling quite high. It should be noted that in the cluster 5, also originating in Asia positive trend is the least as the air is sampled in the higher latitudes. In general the closer the origin area to Europe is, the smaller are the positive trends.

In most clusters ozone trends seasonality (except for the clusters 5 and 7) is characterized by the strongest positive trend in spring. The most local clusters 4 (Europe) and 7 (Central Atlantic) are characterized by the lowest among the other clusters spring trend. On average, air arriving in these two clusters has the least often contact with

UTLS (5.2% and 4.6% of cases, respectively). On the other hand even stratospheric air in these clusters is sampled in the other geographical regions in comparison with the clusters of longer length. It is likely that more substantial change (increase) of STE occurred closer to the US coast, but not over Europe (we could see above analyzing FT and long-range transport cases at KHMS). Moreover, considering the clusters which center is situated to the North of the pathways of the other clusters (cluster 5) and which has quite high number of contacts with UTLS (12.6%) we do not observe an increase in spring, moreover, the spring trend in cluster 5 is close to 0.

Central Atlantic (cluster 7) trends are rather similar to the ones observed in the local European cluster (cluster 4). In these classes the trends might be viewed as superposition of European emission regulations (more positive in winter, less positive in summer) and the general increase of the ozone levels in the Atlantic troposphere. The role of the emission regulations seems to be less important (due to trends similarity in cluster 4 and cluster 7) in comparison with general level increase over Atlantic, but likely important enough to modulate the seasonal shape of the trend.

Comparing the trends in the advection clusters for the later period (1997–2006) with the earlier period (1991–2001, see Tables 9 and 10) the following features can be seen. Annual trends in all clusters become close to 0 with a level of statistical significance comparable to the earlier period. The strongest changes of the trends' values occurred in spring. Proximity of the spring trends to 0 may indicate that the processes, which had provided ozone growth in spring are no longer relevant in the second period, i.e. stratospheric contribution in the upper troposphere is not increasing any more. Nevertheless in winter ozone trends in most of clusters remain positive and statistically significant, being the most positive in the cluster 4 (local European) and cluster 7 (Central Atlantic). Assuming that both of these clusters are substantially impacted by European air we can conclude that in winter the small increase of ozone concentration may be associated with European emissions decrease. Proximity of the summer trends to 0 may also support this conclusion. Among the substantially contributing, only in the cluster 7 (Central Atlantic) summer trend is still positive and statistically significant. This may be connected with increasing ozone production over Atlantic where ship emission are rising (Eyring et al., 2007). Note that summer trend in the cluster, in which air circulates over Europe, is close to zero.

4 Conclusions

Ozone variability at two elevated sites situated in the same latitude belt but at different geographical locations (the Caucasus and the Alps) was compared based on the ozone records at Jungfraujoch (Alps) and at Kislovodsk High Mountain station (Caucasus) covering the period from 1990 to 2006 and belonging to the longest continuous surface ozone series. The sites have substantial difference in altitude (JFJ is situated at 3580 m a.s.l. and KHMS is at 2070 m a.s.l.). In the beginning of the measurements, i.e. 1990–1993, concentrations at KHMS and JFJ are comparable despite of 1500 m difference in altitude. At the end of the period (1998–2005) the annual average difference between ozone levels at two sites is around 15 ppb. In general we found average ozone concentration levels at KHMS (for example in 2001–2004) to be similar to the data reported for the elevated sites of the mid-latitude in Europe and USA, situated in the altitude range from 1600 to 2400 m a.s.l.

Distribution functions of the hourly concentrations were studied for both sites. Ozone distribution at JFJ can be fitted by bi-modal distribution function, while for KHMS the distribution of hourly mean concentrations is closer to the Gaussian function. The primary maxima of the distribution functions are close for two sites, being 45.5 ppb at JFJ and 43.4 ppb at KHMS and comparable to other data, presented in Lee et al. (2007).

Both sites are characterized by the wide spring-summer seasonal maximum. The shape of the seasonal cycle varies from year to year at both locations (JFJ and KHMS) and this variability is possibly caused by variations in global atmospheric dynamics.

Analysis of the 3-D trajectories for the whole measurement period showed that for the subsets more impacted by stratosphere (with PV exceeding 2 PVU along trajectory) the spring maximum is dominating, while summer maximum is more controlled by ozone production in PBL (selected as the cases when trajectory spent more than 2 days of the last five before arrival at the site in the contact with PBL). Analysis of the seasonal cycle for the different horizontal advection clusters showed that spring maximum prevails at both JFJ and KHMS in the clusters associated with long-range transport and originating in the free troposphere above East Asia. In the clusters of the local/regional advection summer maximum is prevailing also at both locations showing the importance of ozone photochemical production in the polluted air masses which were in the contact with European PBL.

The trends of the surface ozone at JFJ and KHMS were studied for two different periods, namely 1991–2001 with strong concentration changes at both stations and 1997–2006, characterized by concentrations stabilization. For the earlier period (1991–2001) trends are substantially negative at KHMS and positive at JFJ. Trends at JFJ have pronounced seasonality being the most positive in spring and the least positive in summer and autumn. In contrary the trends in the 1990s at KHMS are the most negative in summer and the least negative in winter and autumn. For the period 1997–2006 the trends at JFJ are close to 0 on average and for the most of seasons, except for winter when they are still positive and statistically significant. At KHMS the trends remained negative on average and for the most of seasons, except for summer. Seasonality of the trends at KHMS for 1997–2006 is opposite to the one in the earlier period.

To interpret the origin of the trend at each station we used a trajectory analysis. The subsets were organized separating the arriving air masses in accordance with vertical or horizontal air parcels position along the trajectories. So, the cases of the air contact with PBL, with upper free troposphere and stratosphere and having different geographic origin areas were studies separately.

Analyzing different subsets we come to the conclusion that the ozone trends at KHMS in the 1991–2001 are connected with strong emissions reduction in the regions, surrounding station (from local to European scale). This conclusion is supported by the trends value in PBL cases and in the local and European horizontal air advection clusters. Nevertheless, the trend is unlikely to be totally due to regional photochemistry and impact of the other factors is possible (ex., underestimated mixing, difference from JFJ in the areas of the stratospheric air sampling and less frequency of such events). Only the change in emissions is not able to reproduce the magnitude of the negative trends, for example the trends in the subset for the upper troposphere/lower stratosphere and for the clusters of the long-range transport traveling quite high are still negative, while air spent very limited time in the contact with regions of the strong emissions reduction. There are some indirect indications that stratospheric air contribution at KHMS differs from the one at JFJ (negative spring trend in the ozone subset filtered for the cases of PV>2 PVU and p<400 hPa remains nearly invariable between 1991–2001 and 1997–2006) at KHMS.

Positive trends of the surface ozone at JFJ in the 1991–2001 are connected with an increased contribution from the stratosphere over Atlantic, which is confirmed by the analysis of the free tropospheric/stratospheric subsets, by the highest positive trends in the longest and the highest traveling horizontal clusters and by trends seasonality (maximum positive trends are observed in spring). The response to the regional European emissions decrease is less important but it is contributing to the seasonality of the trend. During the later years the trends became close to zero. Increase of the winter concentrations in the later years at JFJ may be connected with emissions regulations as far as decrease in NO titration and decrease in ozone production are likely to occur under this scenario.

It should be noted that the changes in the number of cases of different criteria performability are not able to explain dramatic changes of the trends at the two locations between 1991–2001 and 1997–2006, so the changes in the advection patters can play an important role in the formation of the inter-annual variability but unlikely to impact the systematic ozone changes. The reason of the trends difference at KHMS and JFJ is mainly due to the difference in the position of the stations and difference in the source areas affecting ozone variations in the Caucasus and Alps. Position of KHMS close to the Caucasus Ridge and far from the border of the continent makes this location very sensitive to the wider range of factors, controlling ozone in the continental planetary boundary layer. Both substantial emissions decrease in 1990s due to USSR break down and measures in Europe to control emissions as well as different dynamical processes could be seen at the station creating a complex and not clearly understood tendency. Being higher in altitude and closer to Atlantic ocean JFJ is more sensitive to the background ozone changes in the free troposphere over the ocean, while emission changes can also play some role in the trends formation. Rise of the shipping emissions in Atlantic may be seen more clearly in the coming years in the JFJ ozone levels.

Acknowledgements. The project is supported by the Swiss National Science Foundation (JRP IB7320-110831), the European Commission (Marie-Curie IIF project N 039905 – FP6-2005-Mobility-7) the Russian Foundation for Basic Research (project 06-05-64427 and 06-05-65308) and a research grant of Swiss Federal Institute of Technology, Zurich. We acknowledge the possibility to the use the ozone measurements of Jungfraujoch provided by the Swiss Office BAFU (Bundesamt für Umweltschutz, Environmental Protection Agency of Switzerland).

MAX-PLANCK-GESELLSCHAFT

This Open Access Publication is financed by the Max Planck Society.

References

Andreani-Aksoyoglu, S., Keller, J., Ordóñez, C., Tinguely, M., Schultz, M., and Prevot, A. S. H.: Influence of various emission scenarios on ozone in Europe, Ecol. Model., 217, 209–218, 2008.

Auvray, M. and Bey, I.: Long-range transport to Europe: Seasonal variations and implications for the European ozone budget, J. Geophys. Res., 110, D11303, doi:10.1029/2004JD005503, 2005.

Brönnimann, S., Buchmann, B., and Wanner, H.: Trends in near-surface ozone concentrations in Switzerland: the 1990s, Atmos. Environ., 36 (17), 2841–2852, 2002.

Campana, M., Li, Y., Staehelin, J., Prevot, A. S. H., Bonasoni, P., Loetscher, H., and Peter, T.: The influence of south foehn on the ozone mixing ratios at the high alpine site Arosa, Atmos. Environ., 39(16), 2945–2955, 2005.

Cape, J. N., Methven, J., and Hudson, L. E.: The use of trajectory cluster analysis to interpret trace gas measurements at Mace Head, Ireland, Atmos. Environ., 34(22), 3651–3663, 2000.

Chevalier, A., Gheusi, F., Delmas, R., Ordóñez, C., Sarrat, C., Zbinden, R., Thouret, V., Athier, G., and Cousin, J.-M.: Influence of altitude on ozone levels and variability in the lower troposphere: a ground-based study for western Europe over the period 2001–2004, Atmos. Chem. Phys., 7, 4311–4326, 2007, http://www.atmos-chem-phys.net/7/4311/2007/.

Cristofanelli, P., Bonasoni, P., Carboni, G., Calzolari, F., Casarola, L., Zauli Sajani, S., and Santaguida, R.: Anomalous high ozone concentrations recorded at a high mountain station in Italy in summer 2003, Atmos. Environ., 41, 1383–1394, 2007.

EMEP: Assessment Part I, European Perspective, EMEP, Oslo, 2004.

EMPA: EMPA (Swiss Federal Laboratories for Materials Testing and Research), Technischer Bericht zum Nationalen Beobachtungsnetz für Luftfremdstoffe (NABEL) 2000, Dübendorf, 2000.

Eyring, V., Stevenson, D. S., Lauer, A., Dentener, F. J., Butler, T., Collins, W. J., Ellingsen, K., Gauss, M., Hauglustaine, D. A., Isaksen, I. S. A., Lawrence, M. G., Richter, A., Rodriguez, J. M., Sanderson, M., Strahan, S. E., Sudo, K., Szopa, S., van Noije, T. P. C., and Wild, O.: Multi-model simulations of the impact of international shipping on Atmospheric Chemistry and Climate in 2000 and 2030, Atmos. Chem. Phys., 7, 757–780, 2007, http://www.atmos-chem-phys.net/7/757/2007/.

Götz, F. W. P. and Volz, T.: Aroser Messungen des Ozongehaltes in der unteren Troposphäre und sein Jahresgang, Z. Naturforsch., 6a, 634–639, 1951.

Helmig, D., Oltmans, S. J., Carlson, D., Lamarque, J.-F., Jones, A., Labuschagne, C., Anlauf, K., and Hayden, K.: A review of surface ozone in the polar regions, Atmos. Environ., 41(24), 5138–5161, 2007.

Henne, S., Furger, M., and Prevot, A. S. H.: Climatology of mountain venting-induced elevated moisture layers in the lee of the Alps, J. Appl. Meteorol., 44, 620–633, 2005.

Henne, S., Furger, M., Nyeki, S., Steinbacher, M., Neininger, B., de Wekker, S. F. J., Dommen, J., Spichtinger, N., Stohl, A., and Prévôt, A. S. H.: Quantification of topographic venting of boundary layer air to the free troposphere, Atmos. Chem. Phys., 4, 497–509, 2004, http://www.atmos-chem-phys.net/4/497/2004/.

Goskomstat: Information of the Goskomstat of Russia, Financial- Economical Bulletin of Oil and Gas Industry, N 4, 1999.

IPCC: Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Core Writing Team, edited by: Pachauri, R. K. and Reisinger, A., IPCC, Geneva, Switzerland, 104 pp., 2007.

Jaffe, D. and Ray, J.: Increase in surface ozone at rural sites in the western US, Atmos. Environ. 41 (26), 5452–5463, 2007

Jonson, J. E., Simpson, D., Fagerli, H., and Solberg, S.: Can we explain the trends in European ozone levels?, Atmos. Chem. Phys., 6, 51–66, 2006, http://www.atmos-chem-phys.net/6/51/2006/.

Klausen, J., Zellweger, C., Buchmann, B., Hofer, P.: Uncertainty and bias of surface ozone measurements at selected Global Atmospheric Watch sites, J. Geophys. Res, 108(D19), 4622, doi:10.1029/2003JD003710, 2003.

Lee, H. N., Tositti, L., Zheng, X., and Bonasoni, P.: Analyses and comparisons of variations of ^{7}Be, ^{210}Pb, and ^{7}Be/^{210}Pb with ozone observations at two Global Atmosphere Watch stations from high mountains, J. Geophys. Res., 112, D05303, doi:10.1029/2006JD007421, 2007.

Linvill, D. E., Hooker, W. J., and Olson, B.: Ozone in Michigan's Environment 1876–1880, Mon. Weather Rev., 108, 1883–1891, 1980.

Logan, J. A.: Tropospheric Ozone: Seasonal Behavior, Trends, and Anthropogenic Influence, J. Geophys. Res., 90(D6), 10463–10482, 1985.

Monks, P. S.: A review of the observations and origins of the spring ozone maximum, Atmos. Environ., 34(21), 3545–3561, 2000.

Nolle, M., Ellul, R., Ventura, F., and Güsten, H.: A study of historical surface ozone measurements (1884–1900) on the island of Gozo in the central Mediterranean, Atmos. Environ., 39(30), 5608–5618, 2005.

Oltmans, S. J., Lefohn, A. S., Harris, J. M., Galbally, I., Scheel, H. E., Bodeker, G., Brunke, E., Claude, H., Tarasick, D., Johnson, B. J., Simmonds, P., Shadwick, D., Anlauf, K., Hayden, K., Schmidlin, F., Fujimoto, T., Akagi, K., Meyer, C., Nichol, S., Davies, J., Redondas, A., and Cuevas, E.: Long-term changes in tropospheric ozone, Atmos. Environ., 40, 3156–3173, 2006.

Ordóñez, C., Mathis, H., Furger, M., Henne, S., Hüglin, C., Staehelin, J., and Prévôt, A. S. H.: Changes of daily surface ozone maxima in Switzerland in all seasons from 1992 to 2002 and discussion of summer 2003, Atmos. Chem. Phys., 5, 1187–1203, 2005, http://www.atmos-chem-phys.net/5/1187/2005/.

Ordóñez, C., Brunner, D., Staehelin, J., Hadjinicolaou, P., Pyle, J. A., Jonas, M., Wernli, H., and Prévôt, A. S. H.: Strong influence of lowermost stratospheric ozone on lower tropospheric background ozone changes over Europe, Geophys. Res. Lett., 34(7), L07805, doi:10.1029/2006GL029113, 2007.

Scheel, H. E.: Ozone Climatology Studies for the Zugspitze and Neighbouring Sites in the German Alps, TOR-2 Final Report, 134–139, 2003.

Schnadt Poberaj, C., Staehelin, J., Brunner, D., Thouret, V., and Mohnen, V.: A UT/LS ozone climatology of the nineteen seventies deduced from the GASP aircraft measurement program, Atmos. Chem. Phys., 7, 5917–5936, 2007, http://www.atmos-chem-phys.net/7/5917/2007/.

Schuepbach, E., Friedli, T. K., Zanis, P., Monks, P. S., and Penkett, S. A.: State space analysis of changing seasonal ozone cycles (1988–1997) at Jungfraujoch (3580 m above sea level) in Switzerland, J. Geophys. Res., 106(D17), 20413–20427, 2001.

Senik, I. A. and Elansky, N. F.: Surface Ozone Concentration Measurements at the Kislovodsk High-Altitude Scientific Station: Temporal Variations and Trends, Izvestiya, Atmos. Ocean. Phys., 37, Suppl. 1, S110–S119, 2001.

Senik, I. A., Elansky, N. F., Belikov, I. B., Lisitsyna, L. V., Galaktionov, V. V., and Kortunova, Z. V.: Main Patterns of the Temporal Variability of Surface Ozone in the Vicinity of the Town of Kislovodsk at 870 and 2070 m above Sea Level, Izvestiya, Atmos. Ocean. Phys., 41, Suppl. 1, 67–79, 2005.

Simmonds, P. G., Derwent, R. G., Manning, A. L., and Spain, G.: Significant growth in surface ozone at Mace Head, Ireland, 1987–2003, Atmos.Environ., 38(28), 4769–4778, 2004.

Staehelin, J., Thudium, J., Bühler, R., Volz, A., and Graber, W.: Surface ozone trends at Arosa (Switzerland), Atmos. Environ., 28, 75–87, 1994.

Stevenson, D. S., Dentener, F. J., Schultz, M. G., et al.: Multimodel ensemble simulations of present-day and near future tropophsheric ozone, J. Geophys. Res., 111, D08301, doi:10.1029/2005JD006338, 2006.

Tarasova, O. A., Elansky, N. F., Kuznetsov, G. I., Kuznetsova, I. N., and Senik, I. A.: Impact of air transport on seasonal variations and trends of surface ozone at Kislovodsk High Mountain stations, J. Atmos. Chem., 45, 245–259, 2003.

Tarasova, O. A., Brenninkmeijer, C. A. M., Jöckel, P., Zvyagintsev, A. M., and Kuznetsov, G. I.: A climatology of surface ozone in the extra tropics: cluster analysis of observations and model results, Atmos. Chem. Phys., 7, 6099–6117, 2007, http://www.atmos-chem-phys.net/7/6099/2007/.

Thouret, V., Cammas, J.-P., Sauvage, B., Athier, G., Zbinden, R., Nédélec, P., Simon, P., and Karcher, F.: Tropopause referenced ozone climatology and inter-annual variability (1994–2003) from the MOZAIC programme, Atmos. Chem. Phys., 6, 1033–1051, 2006, http://www.atmos-chem-phys.net/6/1033/2006/.

Tropospheric Ozone Research (TOR-2): in: Towards Cleaner Air for Europe – Science, Tools and Applications, Part 2. Overviews from the Final Reports of the EUROTRAC-2 Subprojects, edited by: Midgley, P. M. and Reuther, M., Margraf Verlag, Weikersheim, 2003.

van der A, R. J., Eskes, H. J., Boersma, K. F., van Noije, T. P. C., van Roozendael, M., De Smedt, I., Peters, D. H. M. U., and Meijer, E. W.: Trends, seasonal variability and dominant NO_x source derived from a ten year record of NO_2 measured from space, J. Geophys. Res., 113, D04302, doi:10.1029/2007JD009021, 2008.

Vingarzan, R.: A review of surface ozone background levels and trends, Atmos. Environ., 38, 3431–3442, 2004.

Wang, T., Wong, H. L. A., Tang, J., Ding, A., Wu, W. S., and Zhang, X. C.: On the origin of surface ozone and reactive nitrogen observed at a remote mountain site in the northeastern Qinghai-Tibetan Plateau, western China, J. Geophys. Res., 111, D08303, doi:10.1029/2005JD006527, 2006.

Wernli, H. and Davies, H.: A Lagrangian-based analysis of extratropical cyclones, 1, The method and some applications, Q. J. Roy. Meteor. Soc., 123, 467–489, 1997.

Zanis, P, Ganser, A., Zellweger, C., Henne, S., Steinbacher, M., and Staehelin, J.: Seasonal variability of measured ozone production efficiencies in the lower free troposphere of Central Europe, Atmos. Chem. Phys., 7, 223–236, 2007, http://www.atmos-chem-phys.net/7/223/2007/.

Zbinden, R. M., Cammas, J.-P., Thouret, V., Nédélec, P., Karcher, F., and Simon, P.: Mid-latitude tropospheric ozone columns from the MOZAIC program: climatology and interannual variability, Atmos. Chem. Phys., 6, 1053–1073, 2006, http://www.atmos-chem-phys.net/6/1053/2006/.

Zellweger, C., Forrer, J., Hofer, P., Nyeki, S., Schwarzenbach, B., Weingartner, E., Ammann, M., and Baltensperger, U.: Partitioning of reactive nitrogen (NO_y) and dependence on meteorological conditions in the lower free troposphere, Atmos. Chem. Phys., 3, 779–796, 2003, http://www.atmos-chem-phys.net/3/779/2003/.

Table 1. Summary of the position of the measuring sites and statistical characteristics of the hourly averaged surface ozone concentration based on the measurements in 1990–2006 at JFJ and KHMS. The last two columns show the statistical characteristics of ozone variability at JFJ and KHMS for the period 2005–2006 (marked with [a]).

	JFJ	KHMS	JFJ*	KHMS*
latitude, N	46.55	43.70		
longitude, E	7.98	42.70		
altitude, m a.s.l.	3580	2070		
N valid measurements (%)	93	66	94	80
minimum, ppb	2.9	3.2	17.6	3.6
maximum, ppb	295.6	113.3	93.3	113.3
mean, ppb ($\pm\sigma$)	51.1 ($\pm$10.5)	43.7 ($\pm$8.7)	52.8 ($\pm$9.5)	40.0($\pm$ 7.9)
variance	109.7	76.2	90.8	63.1
skewness($\pm\sigma$)	0.488 ($\pm$0.007)	0.154 ($\pm$0.008)	0.37 ($\pm$ 0.02)	0.09 ($\pm$0.02)
linear trend based on hourly concentrations ($\pm\sigma$), ppb/year	+0.465 $\pm$0.006	−0.650 $\pm$0.006		

Table 2. Comparison of average ozone concentrations at JFJ and KHMS with observations at the other high altitude sites reported in literature.

site	coordinate	altitude, m	time of measurements	ozone average ($\pm\sigma$), ppb	reference
Davos	46.78° N, 9.82° E	1638	2001–2004	42.0±7.1	Chevalier et al. (2007)
Le Casset	45.0° N, 6.47° E	1750	2001–2004	46.8±7.4	Chevalier et al. (2007)
Arosa	46.77° N, 9.67° E	1840	2001–2004	42.3±8.2	Chevalier et al. (2007)
Wengernalp	46.57° N, 7.12° E	1890	2001–2004	46.8±7.1	Chevalier et al. (2007)
Monte Cimone	44.18° N, 10.70° E	2165	2001–2004	52.8±9.0	Chevalier et al. (2007)
Pic du Midi	42.92° N, 0.08° E	2877	2001–2004	48.3±6.8	Chevalier et al. (2007)
Zugspitze	47.42° N, 10.98° E	2960	2001–2004	51.5±13.7	Chevalier et al. (2007)
Sonnblick	47.05° N, 12.95° E	3106	2001–2004	51.4±6.5	Chevalier et al. (2007)
Jungfraujoch	46.55° N, 7.98° E	3580	2001–2004	53.3±6.8	Chevalier et al. (2007)
Kislovodsk HMS	43.7° N, 42.7° E	2070	2001–2004[a]	42.2±7.8	this study
Lassen N.P., CA	40.51° N, 121.61° W	1756	10/87–8/04	43.3[b]	Jaffe and Ray (2007)
Rocky Mt. N.P., CO	40.31° N, 105.61° W	2743	1/87–11/04	47.2[b]	Jaffe and Ray (2007)
Yellowstone N.P., WY	44.61° N, 110.41° W	2400	4/87–8/04	43.6[b]	Jaffe and Ray (2007)
Pinedale, WY	42.91° N, 109.81° W	2388	1/89–12/04	49.3[b]	Jaffe and Ray (2007)
Gothic, CO	39.01° N, 107.01° W	2926	7/89–12/04	51.0[b]	Jaffe and Ray (2007)
Centennial, WY	41.41° N, 106.21° W	3178	7/89–12/04	51.1[b]	Jaffe and Ray (2007)
Craters of the Moon, ID	43.51° N, 113.61° W	1815	10/92–12/04	44.0[b]	Jaffe and Ray (2007)
Canyonlands N.P., UT	38.51° N, 109.81° W	1809	8/92–12/04	48.0[b]	Jaffe and Ray (2007)
Jungfraujoch	46.55° N, 7.98° E	3580	1/90–12/04[c]	51.0±10.2	this study
Kislovodsk HMS	43.70 N, 42.70° E	2070	1/90–12/04[c]	43.9±8.7	this study

[a] Selected subset (overlapping time period)

[b] For American sites daytime data (10:00–18:00 LST) are reported

[c] Similar to the American sites the day hours only (10:00–18:00 LST) are selected

Table 3. Comparison of trends with 1σ standard deviation for different vertical subsets at KHMS for the period 1991–2001 (average monthly frequency is given in the brackets in %).

	annual	DJF	MAM	JJA	SON
original data set monthly mean	−0.91±0.17	−0.60±0.24	−0.98±0.25	−1.16±0.33	−0.64±0.27
FT cases					
$p<400$ hPa	−0.96±0.18 (17.8)	−0.61±0.26 (19.6)	−1.09±0.27 (18.1)	−1.14±0.36 (11.4)	−0.74±0.30 (22.0)
$p<500$ hPa & PV>1.3 PVU	−0.79±0.20 (7.1)	−0.37±0.28 (9.7)	−0.75±0.27 (7.7)	−0.98±0.42 (3.4)	−0.68±0.31 (7.7)
$p<500$ hPa & PV>1.6 PVU	−0.82±0.20 (5.5)	−0.48±0.29 (7.8)	−0.71±0.29 (5.4)	−1.15±0.42 (2.7)	−0.64±0.35 (5.6)
$p<500$ hPa & PV>2 PVU	−0.78±0.21 (4.4)	−0.57±0.30 (6.1)	−0.67±0.29 (4.3)	−0.95±0.50 (2.4)	−0.70±0.42 (4.3)
PBL cases					
more than 1 contact with PBL east of 10° W	−0.84±0.18 (69.6)	−0.58±0.25 (41.9)	−0.86±0.25 (84.2)	−1.17±0.33 (93.3)	−0.52±0.27 (58.9)
2 of the last 5 days in contact with PBL	−0.82±0.20 (15.8)	−0.67±0.27 (9.8)	−0.81±0.33 (15.0)	−1.12±0.34 (26.3)	−0.49±0.35 (11.6)

Table 4. Comparison of trends with 1σ standard deviation for different vertical subsets at KHMS for the period 1997–2006 (average monthly frequency is given in the brackets in %).

	annual	DJF	MAM	JJA	SON
Original data set monthly mean	−0.37±0.14	−0.30±0.25	−0.20±0.20	−0.14±0.24	−0.60±0.21
FT cases					
$p<400$ hPa	−0.30±0.15 (15.3)	−0.47±0.28 (18.4)	−0.19±0.22 (15.8)	−0.04±0.25 (10.3)	−0.49±0.20 (17.1)
$p<500$ hPa & PV>1.3 PVU	−0.41±0.17 (5.9)	−0.51±0.29 (8.2)	−0.58±0.30 (6.5)	0.00±0.35 (2.8)	−0.43±0.21 (6.4)
$p<500$ hPa & PV>1.6 PVU	−0.42±0.18 (4.5)	−0.60±0.31 (6.3)	−0.70±0.35 (4.7)	0.07±0.34 (2.2)	−0.41±0.26 (4.8)
$p<500$ hPa & PV>2 PVU	−0.31±0.18 (3.6)	−0.52±0.31 (4.8)	−0.71±0.36 (3.6)	0.12±0.32 (2.0)	−0.14±0.29 (3.9)
PBL cases					
more than 1 contact with PBL east of 10 W	−0.41±0.16 (69.4)	−0.26±0.30 (40.1)	−0.23±0.20 (82.7)	−0.18±0.25 (93.7)	−0.63±0.24 (61.2)
2 of the last 5 days in contact with PBL	−0.58±0.19 (18.4)	−0.08±0.37 (8.0)	−0.22±0.25 (16.8)	−0.24±0.28 (33.8)	−1.13±0.36 (14.4)

Table 5. Comparison of trends with 1σ standard deviation for different horizontal clusters of the air mass advection at KHMS for the period 1991–2001 (average monthly frequency is given in the brackets as percent of total number of cases).

	annual	DJF	MAM	JJA	SON
cluster 1	−0.70±0.47 (1.4)	0.44±0.59 (1.8)	−1.38±1.04 (1.2)	−4.33±4.43 (1.2)	−0.63±0.87 (1.1)
cluster 2	−0.78±0.18 (16.8)	−0.56±0.25 (22.6)	−1.22±0.31 (17.0)	−0.67±0.35 (9.1)	−0.45±0.29 (18.4)
cluster 3	−0.90±0.21 (21.5)	−0.42±0.29 (9.9)	−0.99±0.32 (17.5)	−1.04±0.38 (40.9)	−0.70±0.36 (17.6)
cluster 4	−0.98±0.18 (23.8)	−0.78±0.26 (25.2)	−0.96±0.30 (26.7)	−1.43±0.39 (18.8)	−0.51±0.28 (24.6)
cluster 5	−0.89±0.17 (29.3)	−0.62±0.25 (26.7)	−0.80±0.24 (31.5)	−1.29±0.33 (28.4)	−0.62±0.30 (30.5)
cluster 6	−1.09±0.36 (1.6)	−0.06±0.36 (2.1)	−1.85±1.00 (1.5)	−1.40±1.09 (1.2)	−1.09±0.73 (1.2)
cluster 7	−0.80±0.22 (8.6)	−0.62±0.26 (13.2)	−0.75±0.29 (7.4)	−1.06±0.51 (3.6)	−1.23±0.39 (8.7)

Table 6. Comparison of trends with 1σ standard deviation for different horizontal clusters of the air mass advection at KHMS for the period 1997–2006 (average monthly frequency is given in the brackets as percent of total number of cases).

	annual	DJF	MAM	JJA	SON
cluster 1	−0.47±0.51 (1.6)	−1.07±0.68 (1.9)	0.44±1.43 (1.3)	no data	−0.68±0.90 (1.2)
cluster 2	−0.36±0.17 (15.1)	−0.48±0.26 (22.5)	−0.19±0.27 (15.5)	0.06±0.36 (7.4)	−0.67±0.27 (14.6)
cluster 3	−0.36±0.17 (23.7)	−0.51±0.30 (8.7)	−0.22±0.23 (19.9)	−0.30±0.29 (43.7)	−0.43±0.28 (21.6)
cluster 4	−0.18±0.15 (23.8)	−0.22±0.25 (25.8)	−0.09±0.27 (25.4)	0.19±0.27 (18.0)	−0.39±0.20 (26.3)
cluster 5	−0.45±0.15 (30.3)	−0.32±0.28 (27.5)	−0.30±0.19 (32.9)	−0.13±0.25 (29.7)	−0.82±0.26 (31.2)
cluster 6	−0.09±0.34 (2.2)	−0.31±0.34 (3.3)	0.29±1.10 (1.5)	−0.03±1.90 (1.7)	0.08±0.55 (1.2)
cluster 7	−0.57±0.22 (7.8)	−0.40±0.25 (13.2)	−0.56±0.32 (5.8)	−0.53±0.41 (2.8)	−0.46±0.36 (6.8)

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀I ▶I

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 7. Comparison of trends with 1σ standard deviation for different vertical subsets at Jungfraujoch for the period 1991–2001 (average monthly frequency is given in the brackets in %).

	annual	DJF	MAM	JJA	SON
original data set monthly mean	0.73±0.20	0.86±0.22	0.98±0.32	0.73±0.23	0.62±0.22
FT cases					
$p<400$ hPa	0.81±0.20 (28.4)	0.93±0.21 (33.3)	1.07±0.34 (24.7)	0.82±0.26 (27.9)	0.68±0.23 (27.8)
$p<500$ hPa & PV>1.3 PVU	0.80±0.22 (10.9)	0.92±0.24 (13.2)	1.13±0.37 (10.7)	0.63±0.25 (8.6)	0.76±0.26 (11.1)
$p<500$ hPa & PV>1.6 PVU	0.80±0.22 (8.4)	0.88±0.23 (10.1)	1.08±0.38 (8.6)	0.71±0.30 (6.4)	0.78±0.25 (8.4)
$p<500$ hPa & PV>2 PVU	0.82±0.22 (6.5)	0.80±0.23 (7.6)	1.14±0.37 (6.7)	0.72±0.33 (5.3)	0.83±0.29 (6.4)
PBL cases					
more than 1 contact with PBL east of 10 W	0.72±0.21 (35.8)	0.78±0.26 (33.7)	0.98±0.32 (41.0)	0.76±0.24 (33.3)	0.66±0.25 (35.3)
2 of the last 5 days in contact with PBL	0.59±0.23 (5.9)	0.92±0.33 (7.2)	0.83±0.33 (6.3)	0.35±0.35 (4.3)	0.40±0.27 (5.9)

Table 8. Comparison of trends with 1σ standard deviation for different vertical subsets at Jungfraujoch for the period 1997–2006 (average monthly frequency is given in the brackets in %).

	annual	DJF	MAM	JJA	SON
original data set monthly mean	0.04±0.21	0.28±0.16	0.08±0.27	0.22±0.22	−0.17±0.26
FT cases					
$p<400$ hPa	0.17±0.23 (29.1)	0.33±0.17 (31.8)	0.13±0.29 (26.8)	0.35±0.24 (27.8)	−0.11±0.28 (30.2)
$p<500$ hPa & PV>1.3 PVU	0.03±0.23 (10.1)	0.35±0.18 (12.1)	0.16±0.31 (10.4)	−0.04±0.24 (7.7)	−0.06±0.29 (10.3)
$p<500$ hPa & PV>1.6 PVU	0.07±0.23 (7.8)	0.44±0.22 (9.5)	0.13±0.33 (8.1)	−0.01±0.24 (5.7)	0.02±0.28 (7.7)
$p<500$ hPa & PV>2 PVU	0.01±0.25 (6.0)	0.47±0.23 (7.2)	0.12±0.33 (6.4)	−0.33±0.42 (4.3)	0.00±0.32 (6.0)
PBL cases					
more than 1 contact with PBL east of 10° W	−0.01±0.22 (35.3)	0.23±0.19 (36.6)	0.16±0.26 (40.0)	0.12±0.24 (31.7)	−0.32±0.30 (33.1)
2 of the last 5 days in contact with PBL	0.18±0.26 (5.5)	0.32±0.28 (7.2)	0.29±0.31 (6.2)	0.15±0.38 (4.1)	−0.03±0.39 (4.5)

Table 9. Comparison of trends with 1σ standard deviation for different horizontal clusters of the air mass advection at Jungfraujoch for the period 1991–2001 (average monthly frequency is given in the brackets). Maximal seasonal trends are highlighted by italic.

	annual	DJF	MAM	JJA	SON
cluster 1	*1.18±0.26* *(3.0)*	*1.12±0.29* *(4.3)*	1.88±0.59 (2.5)	0.84±0.46 (2.1)	*1.16±0.36* *(2.8)*
cluster 2	0.75±0.19 (29.7)	0.81±0.22 (29.2)	1.15±0.36 (29.7)	0.73±0.26 (30.7)	0.59±0.20 (29.0)
cluster 3	0.90±0.27 (2.6)	0.85±0.30 (3.6)	*2.35±0.92* *(2.1)*	0.66±0.46 (1.8)	0.69±0.36 (2.4)
cluster 4	0.62±0.23 (18.6)	0.66±0.25 (14.4)	0.82±0.31 (20.3)	0.69±0.23 (20.9)	0.58±0.32 (18.8)
cluster 5	0.52±0.27 (2.2)	0.71±0.21 (2.8)	−0.01±0.55 (1.6)	0.62±0.57 (1.7)	0.73±0.44 (2.1)
cluster 6	*0.97±0.20* *(16.0)*	0.85±0.22 (21.7)	1.37±0.35 (14.4)	*1.14±0.33* *(12.3)*	0.73±0.24 (15.5)
cluster 7	0.65±0.21 (30.3)	0.86±0.22 (25.8)	0.81±0.32 (32.3)	0.63±0.24 (32.7)	0.53±0.24 (30.6)

Table 10. Comparison of trends with 1σ standard deviation for different horizontal clusters of the air mass advection at Jungfraujoch for the period 1997–2006 (average monthly frequency is given in the brackets). Statistically significant trends are highlighted by italic.

	annual	DJF	MAM	JJA	SON
cluster 1	−0.06±0.27	*0.28±0.22*	−0.29±0.47	0.51±0.65	*−0.37±0.29*
	(3.2)	*(5.0)*	(2.5)	(2.0)	*(3.0)*
cluster 2	0.03±0.21	*0.22±0.16*	−0.04±0.31	0.26±0.27	−0.08±0.25
	(28.7)	*(28.0)*	(28.9)	(30.5)	(27.3)
cluster 3	0.23±0.32	*0.29±0.24*	−0.02±0.50	−0.22±0.75	0.20±0.48
	(2.4)	*(3.4)*	(1.7)	(1.7)	(2.5)
cluster 4	−0.02±0.25	*0.31±0.25*	0.14±0.26	0.08±0.23	−0.41±0.41
	(17.7)	*(14.6)*	(19.4)	(17.9)	(18.9)
cluster 5	0.01±0.29	−0.25±0.31	0.08±0.52	*0.65±0.58*	−0.17±0.36
	(2.1)	(2.7)	(1.8)	*(1.3)*	(2.1)
cluster 6	0.03±0.21	*0.23±0.14*	0.00±0.28	0.18±0.34	−0.13±0.22
	(16.3)	*(22.6)*	(13.6)	(12.6)	(16.5)
cluster 7	0.10±0.23	*0.33±0.18*	0.18±0.28	*0.32±0.25*	−0.18±0.29
	(31.2)	*(24.3)*	(33.7)	*(35.9)*	(30.8)

Fig. 1. Position of the ozone measurement stations which data are used in the paper. The Caucasus region is presented in more details in the upper corner. The map is compiled from two maps of UNEP/GRID-Arendal Maps and Graphics Library (UNEP/GRID-Arendal. The Caucasus ecoregion, topographic map. UNEP/GRID-Arendal Maps and Graphics Library. 2008. Available at: http://maps.grida.no/go/graphic/the-caucasus-ecoregion-topographic-map. Accessed June 12, 2008 and UNEP/GRID-Arendal. How the comb-jelly (Mnemiopsis leidyi) is spreading through European seas (invasive species). UNEP/GRID-Arendal Maps and Graphics Library. 2007. Available at: http://maps.grida.no/go/graphic/how-the-comb-jelly-mnemiopsis-leidyi-is-spreading-through-european-seas-invasive-species. Accessed 12 June 2008).

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◄◄
►►
◄
►
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

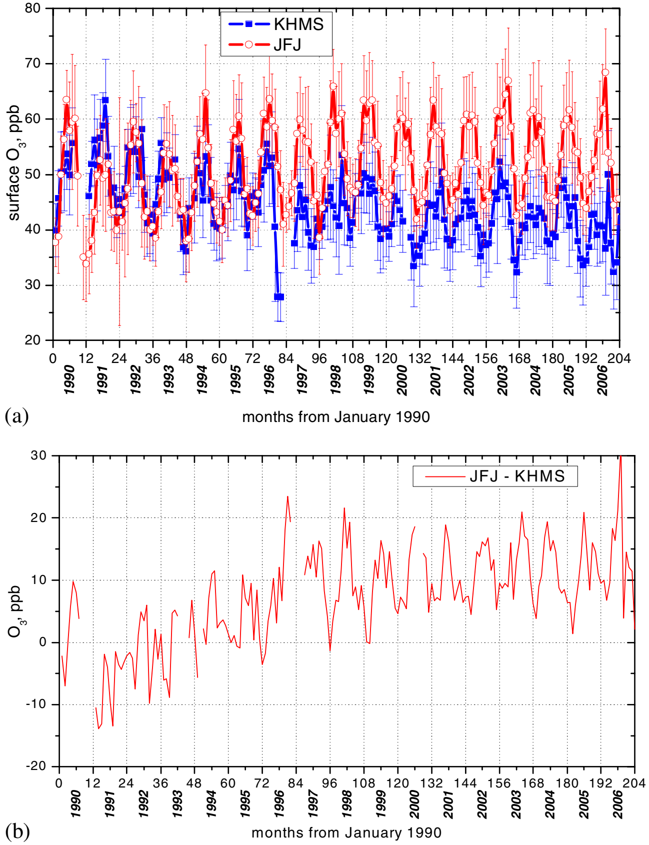

Fig. 2. (a) Monthly mean surface ozone concentrations at KHMS and JFJ, determined from hourly mean values. Plain squares and blue line corresponds to KHMS observations, open circles and red line corresponds to JFJ observations. Error bars show one standard deviation of the monthly mean determination. **(b)** Difference of the monthly mean ozone concentrations at JFJ and KHMS. Note an extreme difference in summer of 2006.

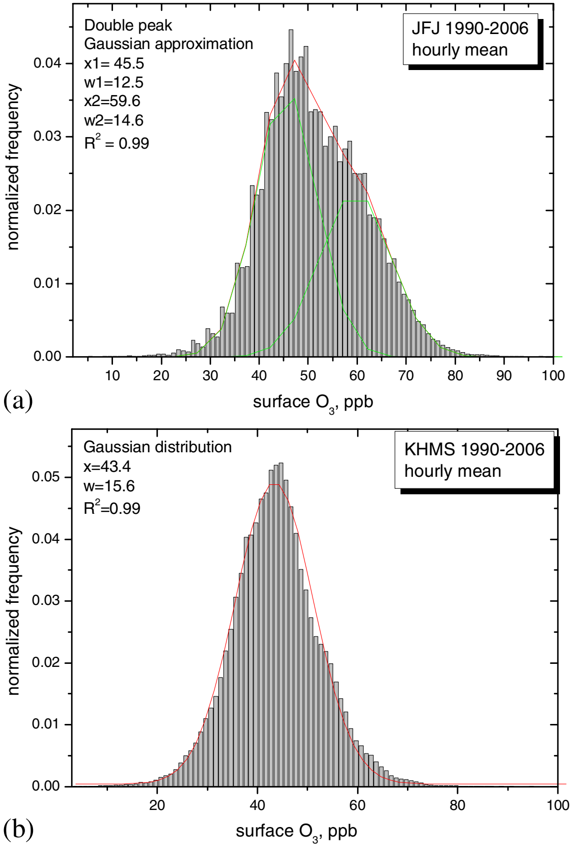

Fig. 3. Distribution functions of the surface ozone concentration at JFJ **(a)** and KHMS **(b)**. Gaussian approximations are given for the distribution functions calculated on the long-term measurements. In the graphs "x" corresponds to the distribution curve center and "w" gives a fit curve width.

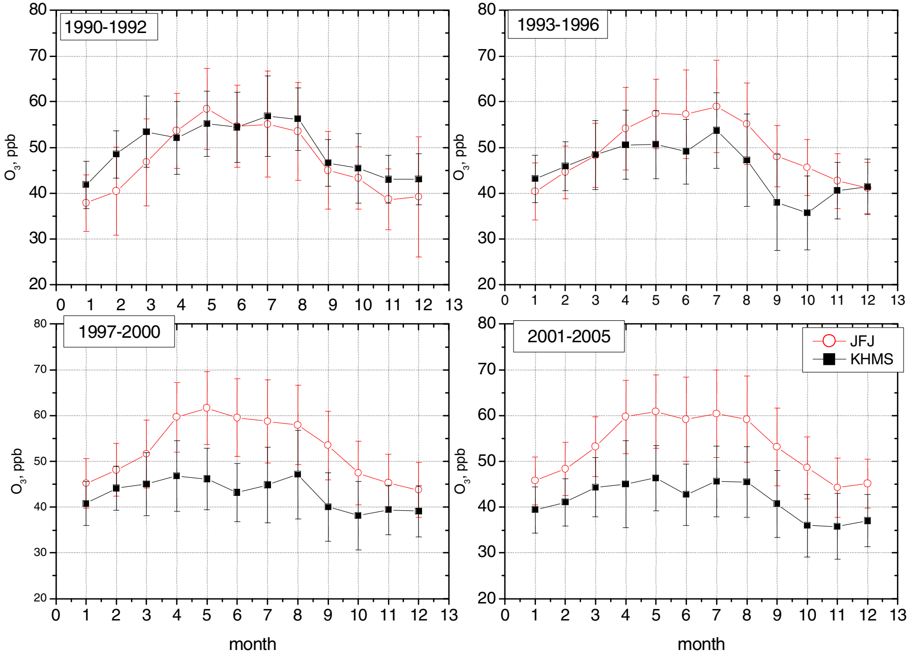

Fig. 4. Comparison of the ozone seasonal cycle at JFJ and KHMS averaged for the different time periods (based on the original hourly mean data). Year 2006 is not included in the last period due to substantially different shape of the seasonal variations at both sites.

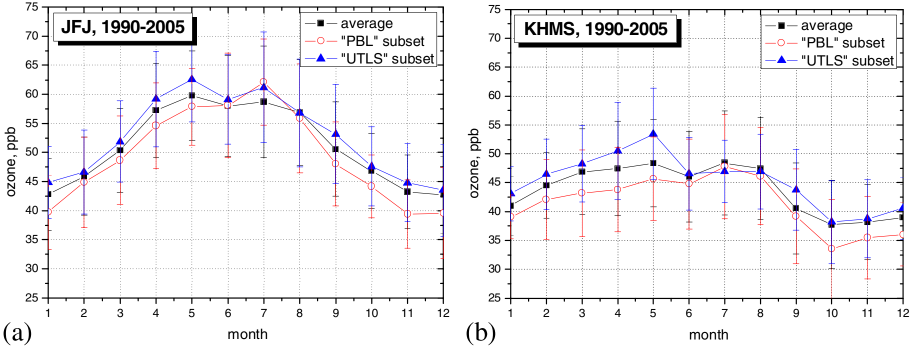

Fig. 5. Averaged ozone seasonal cycles for the subsets filtered on the vertical air mass origin and the average non-filtered seasonal cycles for the period 1990–2005 for JFJ **(a)** and KHMS **(b)**.

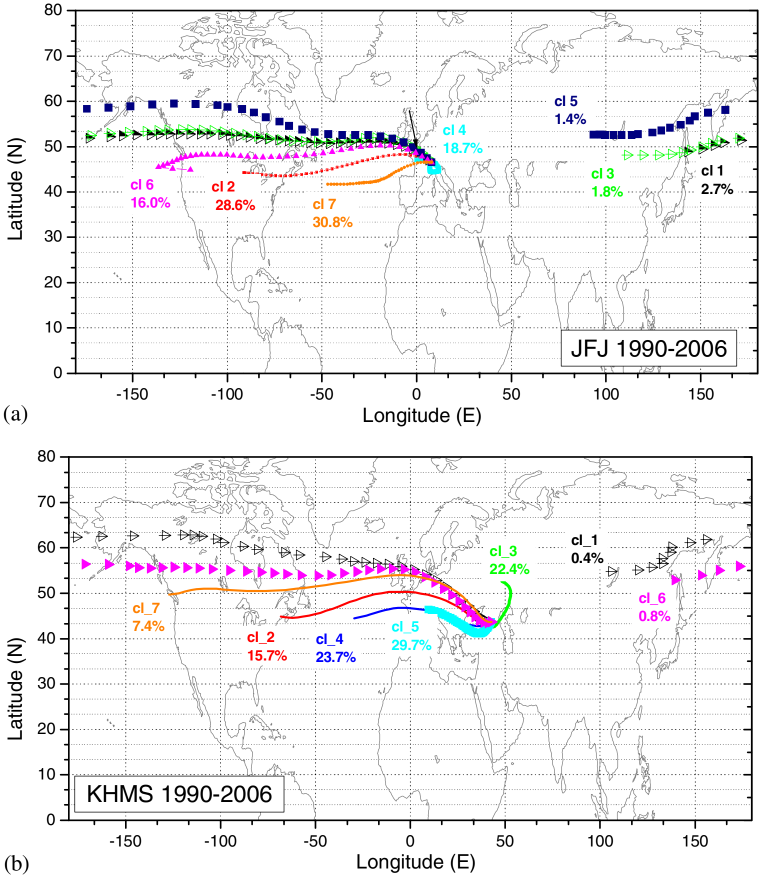

Fig. 6. Centers of the main air transport clusters at JFJ **(a)** and KHMS **(b)** for the period 1990–2006 based on the 3-D LAGRANTO 10 days back trajectories. Numbers at the beginning of the lines show an average frequency to observe the transport in the selected cluster for the whole period. Note that these numbers are seasonally dependent.

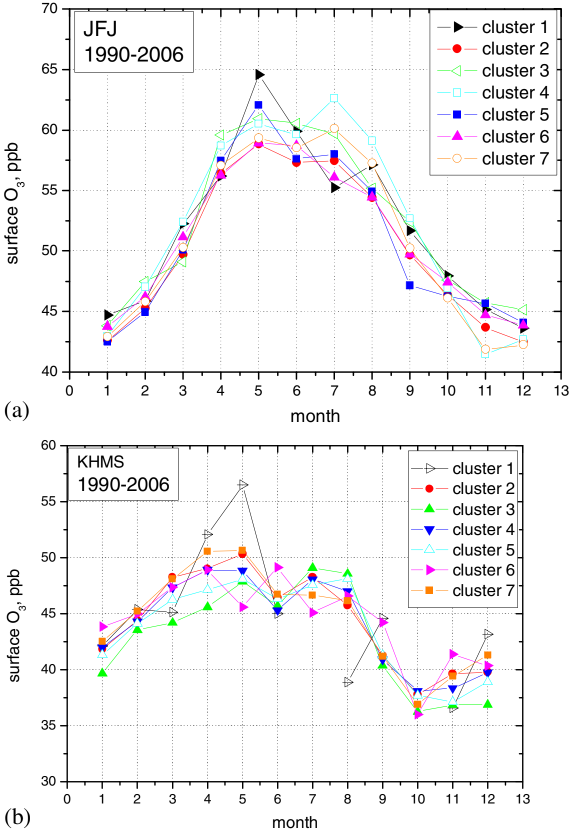

Fig. 7. Averaged seasonal cycles of the surface ozone concentration in the different clusters of the air transport at **(a)** JFJ and **(b)** KHMS. Average cycles are calculated for the period 1990–2006. The colors on the graph are the same as the colors for the cluster centers (Fig. 6). Standard deviations are not shown here to prevent the graphs from overloading with information.

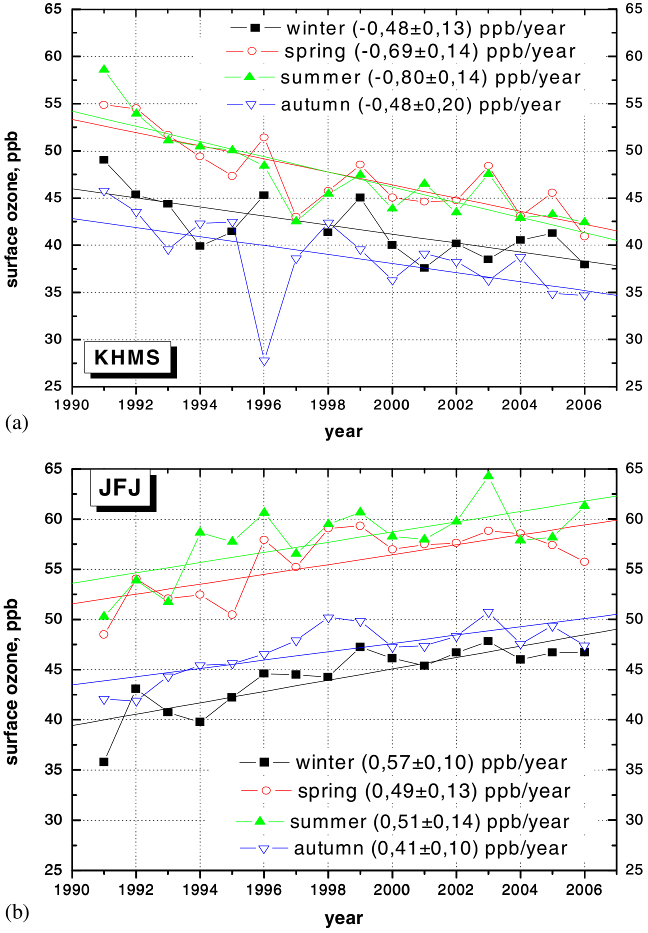

Fig. 8. Seasonally mean surface ozone concentration at KHMS **(a)** and JFJ **(b)** and linear trends for the period 1991–2006.

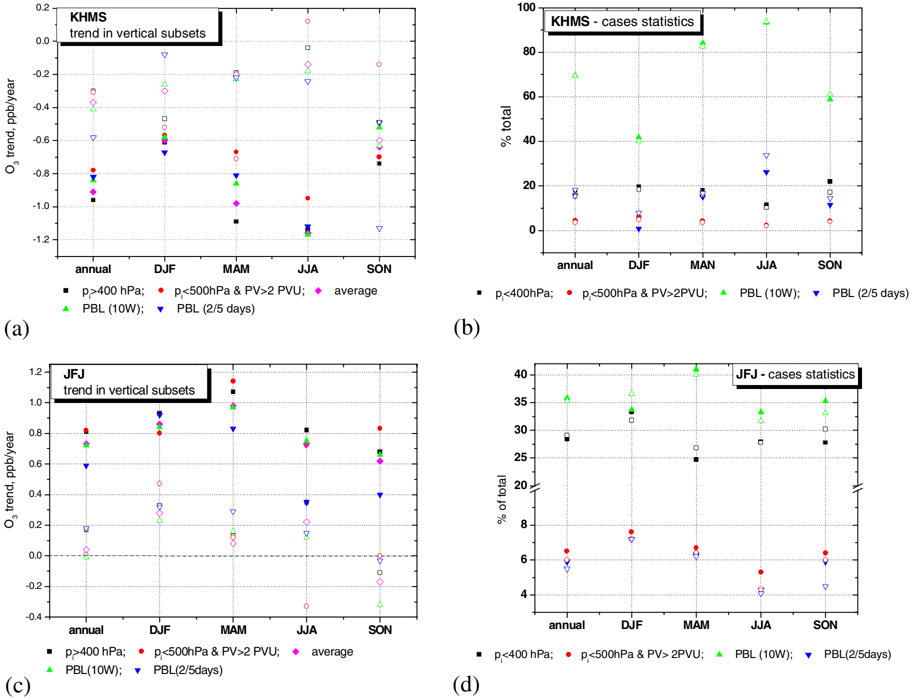

Fig. 9. Trends summary for different vertical subsets (Tables 3, 4, 7, 8) for KHMS **(a)** and JFJ **(c)**. Panels **(b)** and **(d)** show the respective statistics of the cases in which the corresponding criteria given under the plot is fulfilled along the trajectory. The weaker criteria include the stricter ones on the same parameter. Statistics of the FT and PBL cases is presented for different periods in % of the total observational time. More detailed cases encoding is given in the text. For the free troposphere/low stratosphere cases and contact with PBL over the continent total 10 days back trajectories are used, while for the strict PBL contact criterion only 5 days back trajectories are used. Solid symbols correspond to the respective values (trends or cases statistics) in 1991–2001, and open symbols refer to the period 1997–2006.