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Long-term changes in UT/LS ozone between the late 1970s and the 1990s deduced from the GASP and MOZAIC aircraft programs and from ozonesondes

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Abstract

We present ozone measurements of the Global Atmospheric Sampling Program (GASP) performed from four commercial and one research aircraft in the late 1970s to compare them with respective measurements of the ongoing MOZAIC project. Climatologies of UT/LS ozone were built using the aircraft data sets (1975–1979 and 1994–2001), and long-term changes between the 1970s and 1990s were derived by comparison. The data were binned relative to the dynamical tropopause to separate between UT and LS air masses. LS data were analysed using equivalent latitudes. In the UT, pronounced increases are found over the Middle East and South Asia in the spring and summer seasons. Increases are also found over Japan, Europe, and the eastern parts of the Unites States depending on season. LS ozone over northern mid- and high latitudes was found to be lower in the 1990s compared to the 1970s in all seasons of the year. In addition, a comparison with long-term changes deduced from ozonesondes is presented. An altitude offset was applied to the sonde data to account for the slow response time of the ozone sensors. The early 1970s European Brewer-Mast (BM) sonde data agree with GASP within the range of uncertainty (UT) or measured slightly less ozone (LS). In contrast, the 1990s BM sensors show consistently and significantly higher UT/LS ozone values than MOZAIC. This unequal behaviour of aircraft/sonde comparisons in the 1970s and 1990s leads to differences in the estimated long-term changes over Europe: while the comparison between GASP and MOZAIC indicates ozone changes of −5% to 10% over Europe, the sondes suggest a much larger increase of 10%–35% depending on station and season, although statistical significance is not conclusive due to data sample limitations. In contrast to the BM sondes, the Electrochemical Cell (ECC) sonde at Wallops Island, USA, measured higher UT ozone than both GASP and MOZAIC. Hence, long-term changes from GASP/MOZAIC agree within the range of uncertainty with the changes deduced from Wallops Island. The comparison of GASP with BM and ECC ozonesonde data over Europe and the eastern USA, respectively, corroborates earlier studies stating that early

BM instruments measured less ozone than ECC sensor by 10–25%.

1 Introduction

The upper troposphere and lower stratosphere (UT/LS) constitute regions of major concern for both climate impact and the surface environment. Changes in ozone in the LS largely affect the surface UV flux. In addition, because of the radiative properties and temperature structure of the atmosphere, changes in ozone have their largest impact on climate when they occur in the UT/LS (Forster and Shine, 1997).

UT/LS ozone is both determined by transport and chemistry depending on region and season of the year, the relative contributions of different processes is expected to vary strongly across the tropopause. At these altitudes, ozone is produced from precursor substances including nitrogen oxides (NO_x), volatile organic compounds (VOC), and carbon monoxide (CO) under the influence of sunlight and destroyed mainly in reactions with HO_x radicals (e.g., Rohrer, 1995). A relevant natural source of NO_x in the UT/LS is lightning (Schumann and Huntrieser, 2007), while emissions from aircraft constitute an important anthropogenic source. NO_x, VOCs, CO, as well as ozone itself also reach the UT/LS by convective mixing from the boundary layer and upward large-scale transport in the warm conveyor belt parts of midlatitude cyclones (e.g., Stohl et al., 2003). Downward transport from the stratosphere is another important term in the ozone budget of the UT/LS. Any significant long-term change in one of the ozone sources, e.g. in anthropogenic surface NO_x emissions, or changes in the downward flux of ozone from the stratosphere (Collins et al., 2003; Ordóñez et al., 2007), must thus be considered possible causes contributing to UT/LS ozone changes. Several modelling studies emphasize the close relationship between industrial development and changes in tropospheric ozone in large regions of the world (e.g., Levy II et al., 1997; Berntsen et al., 2000; Lelieveld and Dentener, 2000; Fusco and Logan, 2003; Grewe, 2007) indicating that anthropogenic activities significantly contribute to long-term changes of the tropospheric ozone. Knowing how ozone has changed in the troposphere and in the lower stratosphere is therefore of crucial importance for understanding changes in the UT/LS.

Until now, most information on long-term trends in UT/LS ozone is based on regular ozonesonde records from a confined number of stations across Europe, Northern America, and Japan providing measurements back to the late 1960s, more than a decade earlier than the beginning of ozone satellite measurements (e.g., Logan, 1985; 1994; Logan et al., 1999). However, the trends derived from these individual sites may not be representative on a larger, i.e. hemispheric or global scale.

Long-term tropospheric ozone changes largely differ in magnitude and sign in different regions of the world: over Europe and Japan, significant increases were found in the 1970s and 1980s (Logan, 1994), whereas overall trends have levelled off or have become slightly negative since the beginning of the 1990s (Logan et al., 1999; Claude et al., 2004; Jeannet et al., 2007; Oltmans et al., 2006). In Canada, ozonesonde stations changed the sensor type in the late 1970s, which lead to offsets in the time series (Tarasick et al., 1995). Thus, combining the early records from the 1970s with the later observations was judged to be unsuitable for long-term ozone trend analysis. For the period 1980–2001, Canadian tropospheric ozone trends were negative (Tarasick et al., 2005). The same study also indicates that the trends turn positive when considering the period 1991–2001 only. Long-term ozonesonde observations in the United States are available from the Wallops Island station in Virginia with measurements beginning in 1970. In contrast to the changes at the European and Japanese sites, the long-term overall tropospheric change is rather small (<5%) for the period 1970–2003 (Oltmans et al., 2006).

In the LS, large negative trends of more than 5%/decade were found below 18 km over northern midlatitudes for the period up the mid-1990s (WMO, 1992; 1999; SPARC, 1998; Logan et al., 1999). However, ozone trends reported by WMO (2003) for 1980–2000 at 12–18 km were only half as large as those for 1980–1996. Recent estimates of trends in the LS for the period up to 2004 show no decrease at 15 km (WMO, 2007) and ozone mixing ratios at 13–16 km are similar to those in the early 1980s (WMO, 2007;

their Figs. 3–10). The differing trends for the earlier and later periods are due to a decline in ozone during the 1980s and early 1990s followed by a rapid increase thereafter. The eruption of Mt. Pinatubo in 1991 causing enhanced stratospheric aerosol loading and hence increased stratospheric ozone loss in 1992 and 1993, contributed to this evolution (Harris et al., 2008).

Besides balloon profiles, information on UT/LS ozone can be gained from aircraft measurements. This work presents a comparison of ozone measurements from two long-term aircraft programs in the 1970s and 1990s, both providing regular and large-scale ozone measurements of the Northern Hemisphere UT/LS region. The first project, the NASA Global Atmosphere Sampling Program (GASP), was carried out from 1975 to 1979 on four commercial B-747 airliners and one research aircraft to regularly measure ozone and other trace species (e.g., Falconer and Holdeman, 1976; Nastrom, 1977, 1979). Using GASP ozone data, an ozone climatology representative of the second half of the 1970s was derived for the UT and LS regions separately (Schnadt Poberaj et al., 2007, hereafter referred to as SP2007). The second program, the Measurement of Ozone and Water Vapor by Airbus in Service Aircraft Program (MOZAIC) has been in operation since 1994 (Marenco et al., 1998; Thouret et al., 1998a, 1998b, 2006). Within MOZAIC, five commercial aircraft have been equipped with fully-automated instruments to measure ozone and water vapour during in-service flights. The MOZAIC data have recently been evaluated to document substantial increases in tropospheric ozone since 1994 extending from North America over the North Atlantic and Europe to Japan (Zbinden et al., 2006; Thouret et al., 2006).

In this paper, we present UT/LS ozone changes derived from the comparison between GASP and MOZAIC climatologies. For an optimal representation of specific changes in the UT and LS, the analysis separates between tropospheric and stratospheric air masses using local dynamical tropopause information. In addition, we compare long-term ozone changes derived from the aircraft climatologies with those obtained from selected ozonesonde stations.

In the next section, the data sets and methodology used are presented. Section 3 presents the results of UT and LS ozone changes derived from the comparison of GASP and MOZAC aircraft data, and discusses these changes in comparison with respective results from ozonesondes. The last section contains summary and conclusions.

2 Data and methodology

2.1 The GASP and MOZAIC aircraft programs

The GASP program, its ozone measurement system, as well as its quality assurance and control procedures have recently been extensively reviewed by SP2007. Detailed descriptions of the MOZAIC program can be found in a special issue of the Journal of Geophysical Research from 1998 (Marenco et al., 1998; Thouret et al., 1998a, b) and at the MOZAIC website http://mozaic.aero.obs-mip.fr. Only the main characteristics of both programs will thus be summarised here.

Within GASP, four in-service B-747 of United Airlines (1), Pan Am (2) and Qantas (1), as well as the NASA CV-990 research aircraft were equipped with automated instrument platforms to measure ozone, aerosols, condensation nuclei, water vapour, and carbon monoxide. Data are available from March 1975 to June 1979 when the funding for the program was cut. Altogether, the GASP period contains 6149 measurement flights. Measurements were carried out in the middle and upper troposphere and the LS at altitudes between 6 and 13.7 km. The program mostly covered the North Atlantic and Pacific Oceans, as well as the North American continent, but also to a lesser extent Europe (SP2007; their Fig. 1a). A smaller number of flights went to destinations in South Asia, Australia, New Zealand, and South America. On average, eight data records were taken per hour. Assuming the speed of a Boeing 747 to be about 900 km/h at cruise altitudes, this results in in-situ observations at approximately every 110 km.

MOZAIC was launched in January 1993, and has been ongoing since then. Five

Airbus of Air France, former Sabena, Lufthansa (2), and Austrian Airlines have been equipped with fully automated instruments to measure ozone and water vapour during in-service flights. Observational data are available since August 1994. MOZAIC observations cover large parts of North America, Europe, Asia, and also Africa and South America (SP2007; their Fig. 1b). In this study, the pre-processed one minute average data are used for the period of August 1994 through December 2001. Horizontally, the one minute averaging results in a record being representative of approximately 15 km flight path. Between August 1994 and December 2001, 14 558 flights were carried out consisting of 113 008 flight hours. The chosen period ending in December 2001 results from the availability of ECMWF 40-year reanalyses used in this study and the specific processing of the aircraft and ozonesonde data for the separation between troposphere and stratosphere (cf. Sect. 2.3).

The principle of GASP and MOZAIC ozone measurements is a standard ozone monitoring technique based on the absorption of UV light by ozone at 253.7 nm (e.g., Thouret et al., 1998b; Dias-Lalcaca et al., 1998; Klausen et al., 2003). The ratio of the absorption signal, when alternately determining the transmittance of light in a sample of ozone-containing and ozone-free air, yields the ozone concentration making use of the Lambert-Beer law. Note that both GASP and MOZAIC use the same value for the absorption coefficient according to Hearn (1961) (308.5 $\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$). Whereas the GASP instrument was a commercially available ultraviolet (UV) photometer manufactured by Dasibi Environmental Corporation (Tiefermann, 1979), the MOZAIC analyzer is a Thermo-Electron dual-beam UV absorption instrument (model 49-103) (Thouret et al., 1998b).

The GASP data were thoroughly quality checked before use (SP2007; Detwiler et al., 2000): the ozone monitors were exchanged two to four times per year for calibration and functional tests in the laboratory showing that the stability of the instruments' sensitivity over the course of one year changed by less than 1%. Ozone scrubbers were exchanged every three months to prevent degradation with time and hourly in-flights tests were carried out to test the instruments zero with the monitoring over time providing an indication of the instruments' stability. Probably the most critical problem of the GASP system was ozone destruction occurring upstream of the ozone monitor. This was regularly monitored by an ozone-destruction test package, and ozone values were corrected accordingly. As described in SP2007, three major issues had to be treated before using the GASP ozone data: 1.) a general 9% high bias (Tiefermann, 1979) was eliminated, 2.) periods of high frequency sampling (up to 16 samples per minute) were downgraded to one-minute averages from which only a single one-minute average within any five minute interval was stored for consistency with the normal operating procedure. 3.) Erroneous readings that were not flagged in the routine data archival procedure were removed. More details on the pre-processing of the GASP data are given in SP2007.

Concerning MOZAIC quality assurance and control (QA/QC) procedures, the instrument efficiency is checked for drifts during every flight, and ozone analysers are carefully calibrated against a reference analyser on an annual basis (Thouret et al., 1998b). Over the 1994–2001 period, accuracy and precision of the instruments did not exhibit any significant variation (SP2007).

2.2 Ozonesonde data

Ozone profile data from light balloon ascents of the periods 1975–1979 and 1994–2001 have been used for comparison with the aircraft data. The data have been obtained from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) (http://www.woudc.org). Few stations in Europe, Canada, the United States, and Japan provide data records going back to the 1970s. For this study, the European stations Payerne (Switzerland) (Jeannet et al., 2007), the Meteorological Observatory of Hohenpeissenberg (MOHp) (Germany) (Köhler and Claude, 1998), and Uccle (Belgium) (De Backer, 1999), as well as the US American station Wallops Island (Oltmans et al., 1998, 2006) providing a sufficient number of ascents already in the 1970s and consistent time series are considered. An overview of these stations, the number of ascents, and sensor type is given in Table 1. The Japanese stations are excluded as the number of ascents during 1975–1979 is too small to build reliable climatologies. The Canadian stations are not included since the change of sensor type from Brewer-Mast (BM, Brewer and Milford, 1960) to Electrochemical Concentration Cell (ECC, Komhyr, 1969, 1971) at the end of the 1970s leads to significant breaks in the time series (Tarasick et al., 1995). BM instruments were used at MOHp and Payerne throughout both periods. At Uccle, the sensor type was changed to ECC in 1997. To account for this and other changes in the procedures of handling the sensors during more than 30 years of observations, the Uccle time series were homogenised. The data at WOUDC are provided in this homogenised form. A report on the homogenisation procedure can be downloaded from ftp://ftp.kmi-irm.be/dist/meteo/hugo/publ/1999/ (o3prof.pdf) (De Backer, 1999). At the US Wallops Island station, ECC ozone sensors were flown.

The BM sonde data at MOHp and Payerne have been corrected by linear scaling with column ozone measurements, as recommended by the WMO standard procedure for BM sondes. The correction factor (CF), representing the correction applied when comparing the ozone column from integration of the recorded profile and a simultaneous column measurement using a Dobson or Brewer spectrophotometer, was used as quality check. The range of allowed CF has been chosen according to Logan (1994).

At Uccle, as result of the homogenisation, the correction applied to the Uccle data is different from the standard procedure. First, preliminary ozone profiles are calculated including corrections for box temperature, altitude error, SO_2 interference, and background current. However, no pump correction profile is applied. Finally, including correction for the efficiency of the sensor at ground pressure (ground calibration factor), the pump correction values at every pressure level are adjusted such that the profile integral matches the Dobson (before 1984) or Brewer (since 1984) column (De Backer, 1999). This procedure implies that the resulting profiles do not need to be corrected by the standard CF anymore. It may be interesting to note that one of the corrections to obtain the preliminary profile applied to the tropospheric and UT/LS part of the 1970s data was a correction interpreted as negative background current resulting from impurities in the sensor: After a change in preconditioning of the sondes in 1981, it was found that there were discrepancies of 0.3 to 0.4 mPa (i.e., 15–25% at tropospheric and UT/LS levels) in the ascent and descent ratios before and after the change, i.e. the older sondes measured less ozone than the newer sondes. The correction applied approximately equals the mean correction by the standard CF, had it been applied (CF ≈1.2 in 1975–1979). The pump efficiency problems, represented by the altitude dependent correction factors indicated in the WOUDC files, only lead to a correction of 2 to 3% in the UT/LS.

The ECC Wallops Island ascents archived in WOUDC are Dobson normalised for the period 1970–1982, and provided non-normalised afterward (S. Oltmans, personal communication). In many of the latter cases a CF, while existing, is not indicated in the data files. In addition, during both 1975–1979 and 1994–2001, for some ascents normalisation was not possible as Dobson total ozone measurements were not available. In this study, the (1970s) 1990s data were thus (re-)normalised using alternative CFs that are consistent for the whole 1970–2004 Wallops Island record (S. Oltmans, personal communication). This was achieved by using SBUV climatological profiles (McPeters et al., 1997) for the ozone residual at altitudes above 7 hPa or the top of the sounding, if it reached 30 hPa. For the 1970s, the existing normalisation was removed before applying the alternative CFs. Ascents, for which no CFs were available, were treated as having an ideal CF of 1. This is an acceptable simplification as the average CF, calculated from the SBUV dataset, is very near to unity both in 1975–1979 and 1994–2001 (0.99 and 0.983, respectively). Since for a large fraction of ascents, a CF is available (94% and 79% in the 1970s and 1990s, respectively), it can be assumed that on average the CFs of the non-normalised ascents do not significantly deviate from 1 either.

When comparing aircraft UV photometer and balloon data in the UT/LS region, it is of crucial importance to take into account the response time of the sonde sensor, which results in an altitude shift of the balloon vs. the aircraft data. Ignoring the altitude correction may lead to significant errors in the estimated differences between aircraft and balloon ozone in the LS, where vertical ozone gradients are most pronounced. Since the usual practice is not to correct for this lag in response (e.g., SPARC, 1998), we introduce an according correction using the following assumptions: The ozonesonde response time, defined as the time required for the sonde signal to decay by a factor 1/e of its initial value when setting ozone temporarily to zero, has been estimated to approximately 30 s (Smit and Kley, 1998). Assuming an average balloon ascent velocity of 5 ms^{-1} leads to an altitude correction of 150 m. Using the US standard atmosphere (1976), all sonde pressure levels p were converted to altitudes z, which were then shifted downward by the above-indicated distance ($z_{\mathrm{corr}}=z(p)-150$ m) and reconverted in analogous way to corrected pressure levels p_{corr}. Vertical positioning of the ozone data in terms of potential temperature (Sect. 2.3) was obtained by linearly interpolating all potential temperature values $\theta(p)$ to the corrected pressure levels $\theta_{\mathrm{corr}}(p_{\mathrm{corr}})$. Principally, average ozone mixing ratios are increased in a given layer by the altitude shift, the impact being largest at altitudes with maximum vertical gradients. Note that by vertically shifting the profiles, they become inconsistent with sonde integrated ozone and thus with the CF. However, given the applied shift, the effect on sonde integrated ozone and hence the CF is marginal (≈2%).

De Muer and De Backer (1992) showed that their 1970s meteorological sonde (VIZ) recorded smaller geometric altitudes than a radar instrument that was used to track the balloon ascents. For instance, at 10 km altitude, the difference amounted to approximately −100 m (De Muer and De Backer, 1992, their Fig. 3). This effect was accounted for in the homogenisation procedure of the Uccle data by shifting the sonde profiles upward by the difference profile between balloon and radar. However, for consistency with the Payerne and MOHp data, for which a pressure correction was not applied, we have removed this correction by shifting the Uccle sonde data back down by −100 m. This leads to an overall shift of the Uccle 1970s data of −250 m (=ozone sensor response and removing the pressure sensor response: −150 m–100 m). It is generally assumed that the more recent meteorological sondes have no significant pressure response time (W. Steinbrecht, personal communication; De Backer, 1999). For this reason, the Uccle sonde data of the 1990s have only been corrected for the response of the ozone instrument.

2.3 Method of data analysis

The GASP and MOZAIC aircraft and ozonesonde data analysed in this study have basically been processed in the same way as in SP2007. Therefore, only the main features of the methodology will be summarised here: To account for large vertical ozone gradients in the UT/LS, all measurements were scaled against tropopause altitude. To discriminate between tropospheric and stratospheric air, the potential temperature of the dynamical tropopause at 2 PVU was used: Data were assigned tropospheric or stratospheric by calculating the difference between the potential temperatures at cruise altitude, derived from the aircraft data, and at the tropopause, interpolated from fields of the ECMWF reanalyses data set (ERA40, Uppala et al., 2005) (see SP2007). In the LS, all data have additionally been arranged into the equivalent latitude (EL)/potential temperature framework similarly as in Hoor et al. (2004) and Hegglin et al. (2006). In addition, beyond the criteria used in SP2007, the data selection criteria were refined for the purpose of deriving long-term differences:

- UT ozone was not allowed to exceed a seasonally variable upper limit in mixing ratio to avoid aged stratospheric air, mixed into the UT, to significantly bias individual averages in regions with limited sample sizes. This problem especially applies to some parts of the GASP and sonde data. Using probability density functions of UT ozone at middle, subtropical, and tropical latitudes, the upper limit was defined such that at least 95% of the samples were considered tropospheric. This resulted in cutoff values of 80 ppbv, 120 ppbv, 120 ppbv, and 90 ppbv in DJF, MAM, JJA, and SON, respectively.

- Due to the presence of a double tropopause (e.g. a fold), ECMWF potential vorticity interpolated onto the sonde and aircraft positions was occasionally above 2 PVU even when samples were identified as being located below the 2 PVU tropopause. These samples were eliminated from the UT data.

- Only aircraft and sounding data in the pressure range between 330 hPa and 195 hPa (≈8.5 km–11.9 km) were included in the analysis, as this represents the predominant aircraft cruising range (SP2007, their Table 1). For UT analysis, an even narrower range of 330 hPa–235 hPa (≈8.5 km–10.8 km) was selected. The higher levels were excluded as they mostly represent the tropopause region with only little data from the UT.

- Careful pre-processing of the measurement data was also applied concerning the climatological averaging process: In order to increase the weight of measurements taken on different days as compared to the same number of measurements but obtained on a single day, all multi-annual averages were computed from daily means rather than from the individual measurements.

To evaluate differences in UT ozone between 1975–1979 and 1994–2001, differences between climatological seasonal mean averages of both periods were calculated as horizontal distribution on a $10^\circ \times 10^\circ$ map. In addition, to more quantitatively evaluate changes, climatological mean regional averages were calculated for all extratropical regions and the tropical South China region (S CHINA) defined in SP2007. For the tropical region S CHINA, ERA40 pressure at the thermal tropopause was used to identify tropospheric air masses as the 2 PVU tropopause is not suitable in the tropics. An additional region, Middle East (ME), has been included in the analysis due to its importance concerning long-term changes; it extends from 25° N–45° N and 30° E–60° E. For comparison of GASP/MOZAIC with sonde data at Wallops Island (37.9° N, 75.5° W, cf. Table 1), the aircraft data were averaged over 30–50° N and 60–90° W (East USA). This region extends further south than the NE USA region used previously in SP2007 to document the seasonal cycle of UT ozone in the 1970s.

In the LS, the statistics of GASP observations is too limited to allow for a regionally resolved analysis of ozone changes. Instead, quasi-zonal mean differences between MOZAIC and GASP climatological means were calculated as function of EL and potential temperature distance from the tropopause for $5^\circ \times 10\,\mathrm{K}$ grid cells. Longitudinal variability is assumed to be small in this co-ordinate system due to the approximate conservation of PV and potential temperature during transport in the stratosphere and the long lifetime of ozone. To ensure representativeness of GASP (MOZAIC) long-term means, climatological means were only calculated if at least 30 (50) daily means in at least three (six) years were available in every grid box. The methodology leads to sufficiently large GASP samples in most grid boxes. However, distributing the relatively few sonde data of the 1970s over EL results in rather small sample sizes in some grid boxes (<10 daily means). This problem is particularly significant in summer and autumn when the tropopause is high. Still this approach was preferred over further latitudinal averaging due to the presence of pronounced latitudinal gradients in LS ozone.

The confidence intervals, displayed in Figs. 2, 7, 8, 9, and 10 illustrating the significance of the differences between the periods were calculated according to

$$CI = \pm t(P/2, Df) \cdot \sqrt{\sigma_G^2 \big/ n_G + \sigma_m^2 \big/ n_m} \qquad (1)$$

where n_G and n_m denote the sample sizes of GASP and MOZAIC data, respectively, and σ_G^2 and σ_m^2 the sample variances. t designates the cutoff value in a Student's t-distribution depending on a selected probability P=0.05 and the degrees of freedom (Df=n_G+n_m−2).

Over some regions and in some seasons, GASP 1975–1979 climatological means are heavily biased toward the year 1978. This is particularly true for GASP UT ozone over the western and northeastern United States, the Atlantic, Europe, and Northern Japan in summer and autumn (Sect. 3.1). Similar biases also exist for LS ozone in summer, and only at high latitudes >50° N EL, in autumn (Sect. 3.2). There are indications that the year 1978 was exceptional in terms of tropospheric ozone: annual means at Wallops Island showed maximum values in 1977 and 1978 in the sampling record between 1970 and 1995 (Oltmans et al., 1998; their Fig. 2). Less pronounced, but still relatively high annual mean values are also visible in 1978 and 1979 at 500–300 hPa at

MOHp (Oltmans et al., 1998; their Fig. 2). Additionally, the GASP UT time series over Europe show that 1978 summer values were anomalously high in the period 1975–1979 (not shown). Unfortunately, there are not enough GASP summer flights over the eastern USA and the Atlantic during other years than 1978 to confirm the pattern for these regions. Long-term changes in regions with a sampling bias toward the year 1978 therefore need to be interpreted with care.

3 Results and discussion

In this section, changes of UT/LS ozone between the late 1970s and the second half of the 1990s deduced from the GASP and MOZAIC datasets are described separately for the UT (Sect. 3.1) and the LS (Sect. 3.2). Section 3.3 adds a comprehensive comparison with long-term changes deduced for BM and ECC ozonesondes for both LS and UT, and Sect. 3.4 contains the discussion of results.

3.1 UT ozone changes between 1975–1979 and 1994–2001

Long-term relative differences between GASP and MOZAIC UT ozone are shown as horizontal distributions in Fig. 1 and as regional averages in Fig. 2.

Over the western parts of the United States, differences between the climatologies of the 1970s and 1990s lie, on average, within the range of ±5% during all seasons and none of the changes are statistically significant (Fig. 2, W USA). This may not only be due to the relatively small differences, but also related to the limited availability of MOZAIC data for this region. Moreover, note that the summer and autumn changes have been derived from GASP and MOZAIC samples that are strongly biased to one year of data. They may, therefore, not be indicative of long-term changes. Unfortunately, over western North America, there are no other long-term measurements in the UT/LS for comparison. Published information on long-term trends over the western United States is available from a number of surface ozone stations, but only for measurements starting in the 1980s (Jaffe et al., 2003; Jaffe and Ray, 2007). Seven stations indicate statistically significant annual ozone increases for the period 1987–2004 (Jaffe and Ray, 2007), among them the observatory at Lassen Volcanic National Park (40.5° N, 121.6° W). In contrast to the latter station, however, no overall change was observed at the nearby site Yreka over the period 1981–2003 (Oltmans, 2006). Also, evaluating 3–8 km data from the ECC ozonesonde site at Boulder, Colorado (40.0° N, 105.3° W), for the period 1985–2004, no long-term trend could be detected (Jaffe and Ray, 2007), supporting our finding that changes in the free to upper troposphere may have been minor over the Western US.

The picture looks different over the northeastern parts of the USA (NE USA). There, differences between the 1970s and 1990s are mostly positive. Largest positive changes are seen in winter where ozone increased by around 20% on average. Somewhat smaller, but still mostly positive differences of about 10% are found in MAM. In summer and autumn, relative differences are much smaller averaging to a little less than 5% over NE USA, and differences are statistically not or only marginally significant. Note that the GASP data both over the NE USA and ATL regions (cf. discussion below) are strongly biased toward the year 1978 in JJA and SON. Thus, true summer and autumn long-term changes over both NE USA and ATL might be somewhat larger than derived from our analysis.

Similar changes observed at ground stations over NE USA suggest that the UT changes may be related to trends at the surface: The regionally representative station at Whiteface Mountain (44.4° N, 73.9° W, 1480 m) in the eastern United States documents increases of around 4 ppbv (≈10%) over the period 1974–1995 (Oltmans et al., 1998; their Fig. 1). For the same station, but the period 1973–2005, an increase in surface ozone by 12% is reported in the same study. For individual seasons, Oltmans et al. (2006) state significant declines during May and August and increases during December and January. This seasonal dependence is in qualitative agreement with our results showing largest increases in DJF and smallest in JJA. Obviously, wintertime increases at Whiteface Mountain are due to a shift away from lower values in the frequency distribution (Oltmans et al., 2006; their Fig. 12). Such behaviour has also been observed at many stations in Europe and was attributed to the decrease in NO_x emissions resulting in reduced titration of O_3 by NO in wintertime (e.g., Jonson et al., 2006). Evaluating probability density functions of GASP/MOZAIC ozone mixing ratios, a similar pattern is found for Eastern USA (Fig. 3) suggesting a possible link between changes at the surface and those in the UT, probably through fast upward transport. A significant contribution to the wintertime increase in UT ozone concentrations may thus be caused by the reduction of NO_x emissions between the 1970s and 1990s over the United States as can be seen from the RETRO (www.retro.enes.org, Pulles et al., 2007) estimate of anthropogenic NO_x emissions change between 1975–1979 and 1994–2000 (Fig. 4b). A comparison with long-term changes observed at the balloon station Wallops Island, Virginia (37.9 N, 75.5 E), will be discussed in Sect. 3.3.1.

Over the Atlantic (ATL), a relatively similar seasonal change pattern as over NE USA is seen with largest positive changes in the winter season, somewhat smaller, but still mostly positive changes in MAM, and no significant changes in JJA and SON. Only few other observational records exist over the Atlantic region to document long-term changes in tropospheric ozone, which are, moreover, only representative of surface ozone: Ship-borne measurements of the period 1977–2002 do not indicate any significant trend in annual mean surface ozone for the 40° N–60° N latitude interval (Lelieveld et al., 2004). Conversely, ozone measured at Mace Head, Ireland, in air masses originating from the North Atlantic, shows a significant upward trend over the period 1987–2003 (Simmonds et al., 2004). Similar to our results for the UT, the observed increases were largest in the winter season and smallest in summer, again indicating a possible link between lower and upper tropospheric changes, as well as a potential connection to the changes over the northeastern US.

Worldwide air traffic has strongly grown during the last decades (e.g., Schumann, 2002, see also Fig. 4d). Due to its effect of significantly enhancing the abundance of reactive nitrogen (NO_x=NO+NO_2) in the main flight corridors at tropopause altitudes (e.g., Brasseur et al., 1996; Köhler et al., 1997; Schumann et al., 2000) and the impact of NO_x on UT/LS ozone increasing its burden (e.g., Stevenson et al., 1997; Wauben et al., 1997; Dameris et al., 1998; Penner et al., 1999), air traffic increases have to be discussed as one of the likely contributors to long-term ozone increases in the same region. Although NO_x emissions by aircraft contribute only a minor fraction of a few percent to the global NO_x budget from anthropogenic and natural sources (e.g., Lee et al., 1997), their relative contribution is much more significant in the UT/LS of the major flight corridors. Model studies showed that NO_x emissions from aircraft estimated for the early 1990s caused a significant change of the background UT NO_x concentration, which resulted in an ozone increase of 3–8 ppbv in the same region (Penner et al., 1999; Kraabøl et al., 2002; Gauss et al., 2006). If increased air traffic emissions were assumed to be the only mechanism to explain the observed changes, the seasonal dependency of GASP/MOZAIC long-term changes with largest increases in DJF and MAM over NE USA and ATL would speak against a significant influence, as the maximum aircraft effect was predicted for the summer season and the smallest in winter in the before-mentioned studies. However, due to limited data availability in JJA and SON, our analysis yields no definite answer to the true seasonal dependency of long-term changes over NE USA and ATL. In addition, according to Kraabøl et al. (2002), while the maximum effect of aircraft emissions is smaller in winter than in summer, the summer maximum is found at polar latitudes (7–8 ppbv), while increases of similar magnitude are found in the winter and summer seasons at midlatitudes (winter: 3–4 ppbv, summer: 2–5 ppbv). The latter numbers are the same order of magnitude as long-term ozone increases found by GASP/MOZAIC for the winter and spring seasons over NE USA (7–8 ppbv) and ATL (2–6 ppbv) (not shown), which may, acknowledging all above-mentioned uncertainties, nevertheless indicate a connection between air traffic increases and long-term UT/LS ozone in these regions and seasons.

Over Europe, increases are seen in all seasons except in SON (Fig. 1). In DJF, an increase of 5–15% is indicated over the northwestern parts of Europe (45–55° N, 5° W–15° E). However, the average over the EUR region does not show any significant differences (Fig. 2) due to decreases in the southeastern parts of the EUR region

(Fig. 1a). In MAM, increases of 5–50% are found with smaller changes over the north-western parts (5–15%), and larger ones over the eastern parts (50%), and with a mean increase of ≈10%. Except for decreases over Great Britain and the adjacent Atlantic Ocean that are statistically not significant, summertime ozone significantly increased by 10–20% over Europe. In SON, changes amount to less equal than ±10% and are statistically not significant. These latter differences may not be representative, since only three years of GASP data are available over Europe in SON that are additionally strongly biased toward the year 1978.

Other information on long-term free tropospheric ozone trends over Europe is available from a number of stations, such as the high Alpine mountain site Zugspitze, Germany, and the ozonesonde stations at MOHp (Germany), Payerne (Switzerland), and Uccle (Belgium). Zugspitze shows large increases in ozone over the period from 1978–2004 (Oltmans et al., 2006; their Fig. 4). In all months of the year, monthly climatological ozone mixing ratios of 1978–1984 vs. 1995–2004 indicate rather uniform increases of ≈10 ppbv. The differences deduced from GASP/MOZAIC are considerably smaller, they amount to 0–5 ppbv over the EUR average. Changes in the UT derived from ozonesondes will be discussed in detail in Sect. 3.3.1.

The Middle East region is largely unexplored with respect to ozone observations and information on regional long-term changes. Both GASP and MOZAIC (and climatological data from the NOXAR project, see Brunner et al., 2001) aircraft observations point to an UT seasonal cycle that is characterised by a winter minimum and a spring to summer maximum (Fig. 5). While winter values amount to 40–50 ppbv in both periods, summer mixing ratios are as high as 45–75 ppbv in the 1970s and 65–85 ppbv in the 1990s. A summertime maximum is also found in retrievals of satellite measurements (Kar et al., 2002) and in ECC ozonesonde observations from Isfahan, Iran (32.5° N, 51.7° E), for which climatological mixing ratios (period 1995, 1996, and 1999–2005) at 400 hPa amount to approximately 55, 70, 85, and 60 ppbv in DJF, MAM, JJA, and SON, respectively (ozonesonde data available at www.woudc.org). Except for higher summer mixing ratios, sonde measurements compare well with MOZAIC and NOXAR.

There is clear indication that spring and summer UT ozone values have strongly increased over the last two decades: from the horizontal change pattern, increases of 20–50% and 25–45% are deduced for MAM and JJA, respectively. Note that the summertime changes derived from vertically integrated UT ozone may be overestimated by a few percent, as GASP aircraft collected most data at −10 to −20 K below the tropopause, where lower mixing ratios of ∼45 ppbv prevailed, while MOZAIC gathered data also from smaller distances below the tropopause. Thus, the sample contained a larger fraction of data with higher mixing ratios. In autumn and winter, only moderate changes of <±15% are seen in the horizontal change pattern and averaged over the ME region (<10%).

The spring and summer increases in UT ozone are probably related to a combination of causes: First, anthropogenic surface NO_x emissions have vastly increased by 80–300% over the Middle East and India (Fig. 4b). Air traffic NO_x emissions, although representing a minor fraction compared to surface emissions, are estimated to have increased by a factor of 4 from the 1970s to the 1990s over the Middle East and South Asia (Fig. 4d). Thus, it seems plausible that enhanced NO_x abundance has lead to increased photochemical ozone production. However, due to large-scale subsidence in the subtropical high pressure belt, surface air pollution may not easily reach the UT. Therefore, adding to potential effects on regional ozone increases, long-range transport from Europe by the westerly subtropical jet stream in the north of the Middle East and from the Indian subcontinent in easterly flow of the Asian monsoon anticyclone in the south of the Middle East may have principally contributed significantly to the spring and summer increases (Li et al., 2001, their Fig. 3). Both lightning produced NO_x and NO_x from anthropogenic sources over India reaching the UT through monsoonal convection have been discussed to lead to unusually high local UT ozone, which is then transported to the Middle East (Li et al., 2001). The increase in anthropogenic NO_x emissions over India may thus have played a substantial role (cf. below discussion on changes over India).

Over India, large increases of 10–30% are seen in the horizontal distribution in spring

(Fig. 1b). In summer, even larger increases are found ranging from 25 to 60% (Fig. 1c). Averaged over N IND, spring and summertime ozone increased by about 25% and 40%, respectively (Fig. 2). Long-term changes in SON and DJF tend to be positive and indicate more moderate increases than in JJA that are of the order of 5–10%. However, differences are statistically not significant.

The large UT ozone increase over N IND in summer leads to a change in the annual cycle: while in the 1970s, summer values are at minimum in the seasonal cycle, this minimum has disappeared in the 1990s (SP2007, their Fig. 8). A plausible explanation for the apparent change in seasonality could be the drastic increases in ozone precursor emissions over the Indian subcontinent over the last decades (Fig. 4b and d) and an associated increase of tropospheric ozone that has been shown from surface ozone measurements (Naja and Lal, 1996) and from ozonesonde observations at three Indian sites (Saraf and Beig, 2004). In the middle to upper troposphere during 1971–2001, annual increases of 1.4%/yr to 1.8%/yr are found at the balloon stations Trivandrum (8° N, 76° E) and Pune (18° N, 73° E), respectively; very large positive tropospheric trends are found at Delhi (28° N, 77° E) (4–14%/yr) (Saraf and Beig, 2004, their Table 1). The first two numbers agree favourably with summer increases deduced from GASP and MOZAIC for the UT (Fig. 2) that amount to 2.1%/yr over N IND and 1.8%/yr over ME. In fact, it could be shown in a model study of the period 1991–2001 that the largest effect of surface ozone increases over India on UT ozone occurs in the monsoon season when polluted air can be exported to the free and upper troposphere in deep convection (Beig and Brasseur, 2006).

Over Japan, very few aircraft data are available, especially from the GASP program. For this reason, no long-term changes could be derived for the winter season (Fig. 1a). In all other seasons, mostly significant increases are found: 15–25%, 20–30%, and 10–15% in MAM, JJA, and SON, respectively (Fig. 1). When evaluating changes over the N JP and S JP regions separately (Fig. 2), it is important to recall that these regions include data from a relatively large longitudinal range from 115° E to 170° E. Assuming that similar changes can be expected over Japan itself and the adjacent ocean due to eastward advection in midlatitude westerly flow, additional information can be gained for the winter season in S JP. Small increases of ≈10% are found in this way that are, however, on the edge of being statistically significant. Averaged over the N JP and S JP regions, increases of 10% and 15% are found in MAM, while summer increases amount to 35% and 15%, respectively. In SON, over N JP, only very little data are available for the GASP period, that are strongly biased toward 1978. Over S JP, SON UT ozone increased by 10%.

The differences between GASP and MOZAIC data are in qualitative agreement with Japanese ozonesonde records at Sapporo (43° N), Tsukuba (36° N), and Kagoshima (32° N), which document upward annual trends in UT ozone of 5%/decade (or 10% in 20 years) over the period 1970–2004 (Oltmans et al., 2006; their Fig. 9). Lower tropospheric ozone mixing ratios above Sapporo (750–550 hPa) have increased by 13% and 12% in MAM and JJA, respectively, between the periods 1970–1985 and 1986–2002 (Naja and Akimoto, 2004; their Table 2a). These seasonal increases are in reasonable agreement with the spring and summer increases deduced from GASP/MOZAIC for the UT. Long-term changes in the UT and lower troposphere over southern Japan deduced from GASP/MOZAIC and the sonde at Kagoshima, respectively, agree very well: at Kagoshima, ozone increased by 17%, 19%, 16%, and 20% in DJF, MAM, JJA, and SON, respectively. Since ozone precursor emissions have not substantially increased over the last two decades over Japan, but are rapidly increasing over China (Fig. 4b; Ohara et al., 2007), Naja and Akimoto (2004) suggested, using trajectory analysis, that Chinese NO_x emissions could largely be responsible for the increased ozone levels during the 1990s over Southern Japan (Tsukuba, Kagoshima). Ozone levels over northern Japan, in contrast, were found to be dominated by air masses from Eurasia. During late spring and summer, these show an increase in LT ozone during the period 1970 to the 1980s and a slight decrease thereafter (Naja and Akimoto, 2004; their Fig. 12b).

Over Southeast Asia, a region for which other long-term observational records of tropospheric ozone are missing, significant increases are seen in the UT in spring and summer (Fig. 1, 85° E–105° E, 5° N–25° N) that amount to 55% and 15–65%, respectively. Averaged over the S CHINA region (5° N–25° N, 90° E–130° E), mean increases amount to ≈10% and 20%, respectively (Fig. 2). Besides increases in anthropogenic NO_x emissions, biomass burning is known to be an important driver of changes in tropical ozone as large amounts of ozone precursors are released including CO, non-methane hydrocarbons, and NO_x. For instance, Southeast Asian CO emissions from wildfires have recently been estimated to have increased by more than a factor of 3 between the 1970s and the 1990s (Schultz et al., 2008; their Fig. 4) underlining the significance of biomass burning emissions increases for tropospheric ozone trends in this region.

3.2 LS ozone changes between 1975–1979 and 1994–2001

Figure 6 shows long-term changes of quasi-zonal mean LS ozone deduced from the GASP and MOZAIC datasets as function of equivalent latitude (EL) and potential temperature distance from the tropopause for the seasons of the year.

At midlatitudes in the winter and spring seasons, statistically significant decreases on the order of $-15\% < \Delta O_3 < 0$ are found above 10–20 K above the tropopause. Below, mixing of tropospheric air into the lowermost stratosphere occurs (Hoor et al., 2002) resulting in larger variability of ozone values destroying statistical significance. Whereas in winter, the amount of relative decreases increases toward higher latitudes and altitude, largest decreases are seen at lower latitudes <40° N EL in spring. Similar to DJF and MAM, decreases are also found in summer at 50 to 80° N EL, but decreases are smaller ($-10\% < \Delta O_3 < 0$ in more than 90% of grid cells), and statistically significant changes are almost exclusively seen between 15 and 25 K and 50 to 70° N EL. In summer, the difference between the GASP and MOZAIC climatologies may be hampered by the fact that most GASP measurements were collected in 1978 (cf. Sect. 2.3). Thus, the statistical significance of decreases might only feign long-term changes in this particular season. In autumn (Fig. 6d), ozone increased by a few percent in the lowermost stratosphere of the middle latitudes, but changes are statistically insignificant in most grid boxes. At higher altitudes above the tropopause between 55–75° N EL, decreases of −2 to −10% are found. The decreases found in winter and spring are in qualitative agreement with the downward trend between the 1970s and 1990s due to ozone depletion by halocarbons and the fact that downward transport of stratospheric ozone to the lowermost stratosphere is strongest in these seasons.

3.3 Comparison of changes derived by aircraft and ozonesondes

3.3.1 Upper troposphere

For comparison of GASP and MOZAIC with ozonesonde data in the UT, the aircraft data were averaged over the EUR and East USA regions as function of potential temperature distance from the 2 PVU tropopause and compared to respective balloon data of the European (Uccle, MOHp, Payerne) and Wallops Island sounding stations, respectively, averaged over the GASP and MOZAIC observation periods. The vertical layers extend from 0 to −5 K, −5 to −10 K, −10 to −15 K, and −15 to −20 K potential temperature distance from the tropopause corresponding to approximate mean metric distances of −0.9 km, −1.8 km, −2.4 km, and −3 km, respectively.

Figure 7 displays the comparison over Europe. Most aircraft and sonde data are available in the range of 0 to −10 K below the tropopause in the chosen pressure range of 330 hPa to 235 hPa. In these layers, aircraft and sonde agree reasonably well in DJF and SON in the 1970s (Fig. 7, 1975–1979), the average differences mostly lying in the range of ≤±10%. Deviations are somewhat larger in MAM and JJA (except for Uccle in JJA) being on the order of 5–15%. However, differences are generally statistically not or only marginally significant, and no clear dependency of differences on station can be inferred, most probably due to relatively small sample sizes of both aircraft and balloon data. Another factor for the scatter of differences may have been the relatively low precision of BM sondes, which has been estimated ±10–15% even for more recent sensors (Smit and Kley, 1998). Further contemporary information on UV photometer vs. sonde behaviour can only be gained from the Balloon Ozone Intercomparison Campaign (BOIC), carried out between June 1983 and March 1984, where BM instruments were compared with a UV photometer (and ECC sensors) (Hilsenrath et al., 1986). While no direct comparison of BM instruments with the UV photometer used is available, Hilsenrath et al. (1986) illustrate that the MOHp BM sensor measured 10–25% less ozone than the Canadian and Wallops Island ECC instruments at 360–180 hPa. This result can be verified indirectly by comparing the GASP climatology over East USA with data from the ECC station at Wallops Island (see below). Note that discussing the 1970s GASP/sonde differences based on more recent intercomparisons of ozone devices of the 1990s may be problematic due to changes of sondes over time including changes in manufacture (BM sondes), in the preparation procedures (BM sondes) or in the solute concentration (ECC sondes) (e.g., De Backer, 1999; Jeannet et al., 2007).

For the 1994–2001 period, a more consistent behaviour over seasons can be identified (Fig. 7, 1994–2001 and Sondes-MOZAIC): There, all BM sondes measure significantly more ozone than MOZAIC throughout the year. In the upper three layers (0 to −15 K) where most data were gathered, the large part of differences is in the range of 5–10 ppbv at Uccle and MOHp (20–25%, 10–20%, 5–15%, and 20–25% in DJF, MAM, JJA, and SON, respectively). Somewhat larger deviations of about 10–15 ppbv are found for Payerne throughout the year (25–30% in DJF, 20–25% in the other seasons). Evaluating the tropospheric ozone time series at Payerne (Jeannet et al., 2007) may possibly explain the larger offset for this station: when accounting for and subtracting ozone associated with background current, the time series at 700 hPa showed much improved agreement with the surface ozone series at Zugspitze (Jeannet et al., 2007; their Sect. 2.3.6 and their Fig. 2, compare their normal time series (DS-Normal) vs. a version in which pre-flight laboratory calibrations were applied prior to total ozone normalization (DS-N-Cal)). Note, however, that long-term changes would not be altered when calculated using the DS-N-Cal series, as the reduction of ozone due to the background current was estimated to amount to 3 nbar in the 1970s and is close to the same value in the later period (Jeannet et al., 2007; their Sect. 2.3.6).

The differences between MOZAIC and BM sonde measurements found here are of comparable magnitude as those identified at 400 hPa between MOZAIC at Frankfurt, Germany, and MOHp (Thouret et al., 1998b; their Fig. 10 and Plate 1) (5–20 ppbv and 5–45%, respectively). Note that we have compared our results to differences at a lower altitude in Thouret et al. (1998b) since in their analysis no distinction was made between tropospheric and stratospheric air masses.

Relative differences between climatological UT ozone profiles of the 1970s and 1990s (1990s–1970s) derived from GASP/MOZAIC are compared with respective differences from European BM sondes (Fig. 8). In DJF and SON, no significant long-term changes can be detected between the two aircraft climatologies. In the same seasons, at those levels where most data are available (0 to −10 K), sonde differences are clearly larger by 15–30% (DJF) and 20–25% (SON), depending on station. Note, however, that in SON, the differences derived from GASP/MOZAIC should be treated with reserve due to confined GASP data availability in combination with a strong bias toward the year 1978 (cf. Sect. 2.3). In MAM and JJA, slightly larger changes of ≈10% and 5–10%, respectively, are derived from GASP/MOZAIC. In contrast to DJF (and SON), the MAM and JJA aircraft/sonde differences agree within the range of uncertainty (except for Payerne at −5 to −10 K in MAM indicating ≈25% larger differences). It may still be worthwhile noting that while aircraft and sonde changes agree well at half of the levels, sonde differences are considerably larger at the other half (changes larger by 8–12%). In DJF, the methodology of the comparison may also possibly have a small influence on the discrepancies in long-term changes: The comparison of aircraft and sonde differences can be improved by restricting the EUR averaging region to 35–55° N/5° W–25° E, thereby removing some negative differences found between GASP and MOZAIC over southeast Europe. This shifts the GASP/MOZAIC differences by +4–8% to amount to ≈5% between the 1970s and 1990s. However, GASP/MOZAIC changes are still smaller than sonde changes.

At Wallops Island, relatively few data are available for building climatologies (numbers in Fig. 9). This is due to two reasons: 1) the 1970s ascent data are provided in relatively low vertical resolution (annual average of 870 m in the pressure range of

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330 hPa to 235 hPa), and 2) an error occurred when processing ERA40 tropopause information of the years 1999–2001: 95% of all 1999, 25% of all 2000, and 44% of all 2001 auxiliary files were corrupted such that assigning of the data to UT or LS was not possible, and hence these data could not be used. Still, in both periods clear positive deviations of sonde from aircraft data are found. In the 1970s, the Wallops Island sonde measured more ozone than GASP by 5–20 ppbv depending on season (≙10–25%, Fig. 9, 1975–1979). Note that the indicated differences have been estimated from the upper two levels (0 to −10 K) where most data are available (except DJF where only the uppermost level was considered). In the MOZAIC period, sondes show a similar positive bias of about 5–10 ppbv or 5–20% (Fig. 9, 1994–2001). While differences in DJF and SON are comparable in both periods, they are somewhat larger in the 1970s in MAM and JJA.

With respect to the behaviour of the Wallops Island ECC sensor of the 1970s, our findings are similar to those gained at BOIC. There, the Wallops Island sonde also measured up to 20% more ozone in the troposphere than the average of all participating instruments (Hilsenrath et al., 1986). Additionally, when contrasting the GASP with BM and ECC ozonesonde data over Europe and East USA, respectively, the results presented here agree with earlier studies stating that early ECC sensors measured more ozone than BM instruments. The order of magnitude of differences of 10–25% indicated in the literature (Attmannspacher and Dütsch, 1970, 1981; Hilsenrath et al., 1986; Beekmann et al., 1994) is confirmed by this study.

For the 1990s, our results are qualitatively and quantitatively supported by two other studies: Thouret et al. (1998b) compared Wallops Island data of 1980–1993 with MOZAIC profile data at New York for 1994–1995: in the free troposphere, differences mostly lied in the range between 5 and 25%. Analogous comparisons of the ECC sounding stations Palestine (Texas, USA) and Pretoria (South Africa) with MOZAIC profiles at Houston (Texas, USA) and Johannesburg (South Africa), respectively, yielded similar results (Thouret et al., 1998b; their Plate 1). Note also results from a more recent study on long-term trends of North Pacific marine tropospheric ozone at the west coast of North America (D. Parrish, personal communication, 2008): in a comparative evaluation of the ECC balloon time series at Trinidad Head (California, USA) and US west coast MOZAIC airport profiles of the period 1997–2006, the sonde mean was about 6% higher than the MOZAIC average over four airports.

Long-term changes between the 1970s and 1990s derived by GASP/MOZAIC for the East USA region and the Wallops Island station are displayed in Fig. 10. The GASP/MOZAIC differences clearly indicate increases in UT ozone throughout the year of up to 10% depending on season. Changes derived from the Wallops Island data are smaller by 5–10% in MAM and JJA and are comparable in DJF and SON. Note that some averages of the 1970s are strongly biased toward one year, e.g. the Wallops Island 0 to −5 K DJF mean, or the GASP summer and autumn averages (Fig. 9). Thus, those averages may not be representative for the whole 1975–1979 period and the "long-term changes" at these levels may rather reflect year-to-year variability in UT ozone. The possibly slightly smaller differences between aircraft and ECC climatologies in the 1990s than in the 1970s may be related to the small number of data available in the 1970s. Probably more important, however, is the change in the strength in sensing solution, which amounted to 1.5% KI-b (potassium iodide buffer) in 1975–1979 and 1994 and was changed to 1% KI-b in 1995 (with buffer proportional to the original receipt) (F. Schmidlin, personal communication): Surface ozone testing of an ECC sensor in Boulder, Colorado, in 1999 and 2000 against a UV photometric surface ozone analyser showed that the 1% KI-b and 1.5% KI-b solution sondes measured about 7 and 14% higher ozone than the UV photometer (Johnson et al., 2002). These differences agree well with the different biases that we find between balloon and aircraft data in the 1970s and 1990s and may thus explain the differences seen in long-term changes. Hence, the long-term changes and trends derived from Wallops Island station data, that include both periods when the 1.5% KI-b and the 1% KI-b solution were used, may be underestimated by a few percent.

3.3.2 Lower stratosphere

Figures 11–13 and Table 2 show that the aircraft/sonde comparisons of the two periods are clearly different: While in 1975–1979, all BM sonde data agree with GASP in the range of uncertainty or measure slightly less ozone, sondes measure significantly more ozone than MOZAIC in the 1990s (≈5–10% at Uccle, 10–15% at MOHp, and 10–20% at Payerne). Recall that Uccle exchanged their BM sensor for an ECC device in the end of 1997, and that the Uccle time series is homogenised. Thus, while the comparison indicates that Uccle tends to measure more ozone than MOZAIC, it cannot be traced back to whether this is due to the BM or ECC device or both.

Principally, the LS comparison confirms the results from the UT (Sect. 3.3.1). Considering that a) longitudinal variability is largely reduced in the EL framework, that b) GASP LS data coverage is better than in the UT for the EUR region, and that c) the LS differences of the GASP period are consistently negative over large areas in MAM, JJA, and SON (Figs. 11–13 and Table 2), this may be a hint that the BM sondes of the 1970s even measured somewhat less ozone than GASP. From the UT comparison, the conclusion was agreement in the range of uncertainty (cf. Sect. 3.3.1).

The differences found in the aircraft/sonde comparisons of the 1970s and 1990s directly impacts the LS long-term differences deduced from GASP/MOZAIC and sondes (Fig. 6, Figs. 11–13, and Table 2): While from GASP/MOZAIC, slightly negative long-term changes are inferred in all seasons, sonde differences, on average, point to positive changes that vary with season (5–25% at Uccle, 10–40% at MOHp, and 15–25% at Payerne). Note that the large upper number at MOHp (Table 2) has been derived from a very small number of grid boxes just above the tropopause (Fig. 12), which may not be completely representative of the whole LS averaging region. Note that the largest sonde long-term changes are all found in SON indicating that decadal changes are largest in autumn. This result is consistent with GASP/MOZAIC, for which the most positive differences are also found in SON (Fig. 6, Table 2). The changes inferred from balloons are, on average, 5–25%, 15–40%, and 20–25% larger at Uccle, MOHp and Payerne, respectively, than estimated by GASP/MOZAIC.

3.4 Discussion of comparison of changes by aircraft and BM ozonesondes

Changes in the bias between BM balloon and aircraft ozone between the 1970s and 1990s result in differing long-term changes derived from the two types of instruments, the changes from aircraft being generally smaller than from ozonesondes. Since both sondes and MOZAIC data are widely being used to investigate short- and long-term ozone trends in the troposphere and UT/LS (e.g., Thouret et al., 2006; Bortz et al., 2006; Oltmans et al., 2006), it is of great importance to better understand the biases and assess the reliability of the different devices used. Several factors including instrument characteristics of the GASP, MOZAIC, and ozonesonde devices, the use of the correction factor CF to adjust the balloon profiles to an independent total ozone measurement, as well as potential biases related to the methodology will be discussed in the following:

A. *UV photometry.* Principally, the technique of UV photometry measurement of ozone is very accurate and precise and generally judged superior to chemical detection of ozone in iodine/iodide solution as done in ozonesondes. Both GASP and MOZAIC programs carried out extensive quality control checks (Sect. 2.1) ensuring reliable performance of the instruments. Additional information on the performance of the UV analysers can principally be gained from quasi-simultaneous and spatially coinciding measurements by other devices. However, the only other available measurements to compare the GASP data with are from the 1970s ozonesondes at the European and Wallops Island stations, for which the confined number of spatially and temporally overlapping measurements might limit clear statements. For the 1990s and MOZAIC, very good agreement was obtained by two near simultaneous flights by a MOZAIC A340 and a SwissAir B747 aircraft equipped with a UV-ozone instrument within the frame of the NOXAR (Nitrogen Oxides and Ozone along Air Routes) project on 20 December 1995, over the

North Atlantic (Dias-Lalcaca et al., 1998, their Fig. 4). A linear fit through a scatter plot of the closest NOXAR and MOZAIC O_3 measurements showed excellent agreement for the observed range of concentrations: MOZAIC ozone exhibits an average intercept of 1.5 ppbv (±1.5 ppbv) from NOXAR ozone, and features the same slope (0.997 (±0.014)) (Dias-Lalcaca et al., 1998; their Eq. 1). Although this comparison is only based on results from two individual flights, it supports high data quality of MOZAIC (and NOXAR) ozone data.

B. *Laboratory simulations of BM ozonesondes of the 1970s.* Some insights into the specific behaviour of BM ozonesondes of the 1970s are presented in a paper by Tarasick et al. (2002): they carried out laboratory experiments to test the response of their early Canadian sondes in comparison with an ozone calibrator at laboratory temperature and pressure and varying ozone input. They found that sonde behaviour strongly depends on pre-flight preparation procedures: Preparing the BM devices according to the original preparation procedures recommended by the Brewer-Mast company (essentially described in Mueller, 1976), the instruments indicated 10–30% lower ozone than the calibrator in the troposphere. In contrast, for sondes prepared according to Claude et al. (1987), the low bias was much reduced or eliminated. The problem seems to be due to time dependent loss processes that result in a) new BM sondes to show a large increase in sensitivity between successive experiments, b) the response of previously flown sondes to increase slowly with time especially at tropospheric ozone levels, and c) sondes to show an additional slow increase of response with time that is possibly caused by ozone reactions with the phosphate buffer. As consequence, after correction to observed total ozone, the earlier part of a flight yields too low values, while the latter part is too high. Hence, in the altitude range of our analysis (330–195 hPa), after Dobson scaling, BM sondes prepared according to the original procedures should underestimate the ozone concentration by a few to about a little more than 10% (Tarasick et al., 2002; their Fig. 7). By simulating a typical variation in ozone experienced by a sonde in flight, Tarasick et al. (2002) could show that this behaviour can explain the average CF (1.255) encountered for the Canadian BM record of the 1970s and the discrepancy in tropospheric measurements.

The behaviour of the early Canadian BM sondes can probably explain the characteristics of those early European BM sondes that were also prepared according to the original BM procedures. This applies to both the Uccle and Payerne stations, while MOHp already prepared their instruments according to Claude et al. (1987) (W. Steinbrecht, personal communication). It can thus be assumed that the Uccle and Payerne sondes faced similar problems as the Canadian devices. In fact, comparing ascent and descent ratios before and after changing the preconditioning of the Uccle sondes in 1981, the instruments before 1981 were identified to measure too low ozone concentrations in the troposphere (De Backer, 1999). De Backer (1999) suspected impurities in the sensor to cause ozone losses that lead to too low ozone values. The problem was accounted for in the homogenisation procedure (cf. Sect. 2.2). The behaviour of the Payerne instrument of the 1970s should also be similar to the Canadian device. The average CF of the ascents used in this study is 1.21, a very similar value as obtained for the Canadian sondes. In contrast, the altitude dependent response of the MOHp sensor should, according to laboratory experiments in the 1990s, be near one throughout troposphere and stratosphere (Smit and Kley, 1998; see discussion under C.). However, as already stated in Sect. 3.3.1, systematic differences in sonde behaviour, expected to be on the order of up to 10%, of the Payerne vs. the MOHP and Uccle devices (Fig. 7) cannot be inferred from our analysis. Still, the fact that the early BM sondes measured somewhat less (Sect. 3.3.2) or comparable concentrations in UT/LS ozone than GASP (Sect. 3.3.1) seems plausible against the background of the theoretical considerations by Tarasick et al. (2002).

C. *Laboratory simulations of the MOHp BM sonde of the 1990s.* To test the behaviour of currently used sonde types (BM, ECC; Indian, and Japanese), the Jülich ozonesonde intercomparison experiment was carried out in 1996 (JOSIE 1996) (Smit and Kley, 1998). Within the frame of JOSIE 1996, intercomparisons between a laboratory UV photometer and the different types of ozonesondes were carried out in the environmental simulation chamber of the World Calibration Facility (WCFOS) at the Forschungszentrum Jülich, Germany. The BM device tested was the original BM instrument from MOHp (prepared according to Claude et al., 1987). To determine precision, accuracy and response of the sondes as function of sonde type, altitude, and ozone concentration, the instruments were tested under a variety of conditions. The results indicate that the MOHp sonde differed from the UV photometer by only −3% ±10 (8) [5]% at 0–5 km (5–10 km) [10–15 km] for a typical midlatitude profile. However, the response of the MOHp BM sonde in the laboratory does not agree with our analyses of Sects. 3.3.1 and 3.3.2, which showed a systematic positive offset from MOZAIC data. This will be discussed further under D.

D. *MOZAIC vs. BM ozonesondes of the 1990s.* While in our analysis (Sect. 3.3.1), we compared climatologies of regionally averaged MOZAIC with respective ozonesonde profiles, Thouret et al. (1998b) compared six individual MOZAIC profiles at Frankfurt (50° N, 9° E) with sonde profiles of the MOHp station (48° N, 11° E) (app. 300 km distance) that had been sampled at the same time (Thouret et al., 1998b; their Fig. 18). While two cases showed remarkable agreement throughout the troposphere, in three of the other four cases the sonde measured higher ozone than MOZAIC in the free troposphere. This comparison, further ones of MOZAIC and MOHp climatologies described in the same publication, and our own analysis of Sects. 3.3.1 and 3.3.2 all indicate that the BM device at MOHp measures, on average, more ozone than MOZAIC in the troposphere and UT/LS. These differences clearly disagree with the results gained at JOSIE 1996 (cf. C.). Additionally, our analysis indicates that the behaviour of the Uccle and Payerne stations is very similar to that of MOHp also showing systematic positive deviations from the aircraft climatology. In respect of the importance of MOHp (and the other long-term BM stations Uccle and Payerne) for deriving long-term changes/trends, it would be essential to understand the different behaviour in the laboratory and in the field to reduce the uncertainty regarding the actual characteristics of the BM sensor.

The differences between average ozone measured by sondes and MOZAIC could also result from principal limitations in the methodology applied in the comparison. Thouret et al. (1998b) discuss several potential reasons for differences including: 1) large distances between airports and sounding stations in combination with large spatial gradients in ozone, and 2) different periods of observation that had been compared. In this study, regional averages of UT aircraft measurements are compared to average balloon profiles of stations located somewhere in this region. Potentially, spatial variations in UT ozone could either bias aircraft or sonde means. However, from the climatological distribution of UT MOZAIC ozone over Europe no significant spatial variations can be inferred in the different seasons except for summer. It is thus very unlikely that the spatial separation between the measurements can explain the observed differences. Even in summer when the spatial variability is largest, the MOZAIC ozone mixing ratios are generally well below the sonde values in the entire EUR region except for a minor fraction of the domain not coinciding with the geographic location of the sounding stations. Moreover, the MOZAIC EUR summer mean agrees favourably with the MOZAIC values found in the vicinity of the stations in the geographical distribution (not shown).

A strong argument for the robustness of the biases of BM sonde vs. MOZAIC ozone and against significant influences by the methodology is the fact that the differences remain when analysing the data in the LS in the EL system, where regional variability at a given EL should be largely suppressed.

E. *On the use of the correction factor CF.* One of the main corrections applied to BM measurements consists of scaling the ozonesonde profiles to an independent measurement of the ozone column carried out by a Dobson or Brewer spectrophotometer (cf. Sect. 2.2). The scaling practice was already introduced in the 1960s, because it was found that the total ozone amount directly inferred from BM sonde

> measurements was about 10% lower than the comparable optically observed total ozone value (Dütsch, 1966). To adjust the balloon data, the CF is multiplied to the whole profile.

The application of the CF has been discussed controversially, since the use of one constant correction value may not be appropriate for the whole profile, and because errors in the total ozone measurement may be passed on to the sonde profile. In particular, errors occurring in the tropospheric measurement are only corrected properly if there is a significant effect on the total ozone measurement and, thus, on the CF. This also means that measurement errors that do not affect sonde column ozone are left uncorrected by the normalisation procedure. For these reasons, and from empirical evidence, it has been recommended more recently by several authors not to use the CF for tropospheric ozone (Beekmann et al., 1995; WMO, 1999; De Backer et al., 1998; Thouret et al., 1998b).

Assuming that the general underestimation of sonde total ozone by BM sondes can mainly be attributed to problems in the stratospheric measurement, it would in fact be more appropriate not to apply the CF for the tropospheric part of the ascents. Indeed, concerning today's BM sondes, Dobson scaling may introduce a small positive bias to tropospheric measurements increasing the ozone concentration by a few percent (Thouret et al., 1998b). Not using the CF, differences between balloon and MOZAIC UT measurements would be decreased and thereby improved by an average of 5% and 7% at MOHp and Payerne, respectively. However, the systematic offset between sonde and MOZAIC data would not be removed completely. Besides the CF, other factors such as pump correction, pump temperature, or background current may systematically bias the ozone profile (e.g., Stübi et al., 2008). However, it is beyond the scope of this publication to investigate these influences, and hence, it remains an open question what causes the discrepancy between today's BM sondes and MOZAIC.

Not applying the CF to the 1970s sondes leads to a reduction of UT ozone by 8% and 21% at MOHp and Payerne, respectively. For MOHp, this results in ozone values that agree or are slightly lower than GASP values ($\geq -10\%$), but are still in the range of uncertainty. Somewhat larger, partly statistically significant negative deviations result for Payerne with differences from GASP ranging from −18 to −3% (not shown). The low bias of the uncorrected Payerne UT data supports the hypothesis that tropospheric ozone measurements of the early data were in fact too low (cf. discussion in C.), and that using the CF may (partly) compensate for this problem. However, note that while the correction using the CF may fit in the UT/LS, it may not be sufficient at other altitudes or conversely overcompensate at still others.

The effect of not considering the CF on long-term ozone changes depends on how the CF has changed over time. At MOHp, no significant change in CF occurred between the 1970s and 1990s, hence not applying the correction does not significantly alter the long-term differences (not shown). At Payerne, however, the CF decreased from 1.21 in 1975–1979 to 1.09 in 1994–2001. Thus, the reduction in differences between MOZAIC and Payerne data in the 1990s is overcompensated by increased differences in the 1970s leading to long-term differences in UT ozone that are increased by 5–15% (not shown). This changes the comparison between aircraft and sonde differences for the worse (cf. Fig. 8) and may represent a long-term increase that is overestimated (see discussion above and C.).

F. *Synthesis of BM and ECC aircraft/sonde intercomparisons.* An indication that the cause(s) for the different long-term changes by GASP/MOZAIC and BM sensors might rather be sought on the ozonesondes' side is given by a comparative evaluation of the BM and ECC aircraft/sonde intercomparisons of both the 1970s and 1990s: despite uncertainty due to sample size restrictions, Wallops Island shows clear and similar positive deviations from the aircraft datasets both in the 1970s and 1990s (Sect. 3.3.1). The behaviour in the two periods is consistent considering the change in the strength of the sensing solution and associated differences in ozone concentrations. As GASP instrument performance can be expected to be the same over East USA and Europe, there is clear indication that the European BM sondes of the 1970s performed differently than the ECC instrument at Wallops Island, with the European BM sondes largely being in agreement with laboratory considerations (cf. B.). Finally, the European BM sondes of the 1990s appear to perform differently than in the 1970s leading back to the unsolved issue why the BM measurements of the 1990s measure higher ozone concentrations than MOZAIC (cf. D.). Assuming the 1970s and 1990s aircraft measurements to be correct, it may be suspected that changes in pre-flight preparation and operating procedures, as well as modifications in the manufacture of ozonesondes might have influenced long-term changes and trends (SPARC, 1998). These theoretical considerations are supported by a statistical study by Hogrefe et al. (1998) who showed that discontinuities existing in ozonesonde time series, among them long-term data from the Payerne and MOHp stations, may significantly affect long-term trend estimates: they conclude that the estimated upward trend in the raw tropospheric ozone data at Payerne and MOHp might at least partly be attributable to the presence of breaks in the data. Hence, gaining better understanding of the discrepancies between sondes/MOZAIC and sonde performance in the 1970s and 1990s is important not only with respect to understanding the decadal ozone trends, but also with respect to improved knowledge of the reliability of the individual instruments. We therefore strongly encourage further laboratory and field intercomparisons of BM ozonesondes vs. UV photometer, as well as coordinated activities to obtain measurements from simultaneous flights by MOZAIC and other aircraft to clarify differences between the different measurement techniques.

4 Summary and conclusions

Differences between climatological UT/LS ozone of the periods 1975–1979 and 1994–2001 were calculated from the datasets of the GASP and MOZAIC aircraft programs to derive long-term changes. These were compared to respective differences deduced from European and one US American long-term ozonesonde stations.

The analysis was separately carried out for the UT and LS using ERA40 dynamical tropopause information, interpolated spatially and temporally to the aircraft and balloon coordinates.

In the UT, differences between the GASP and MOZAIC climatologies were both calculated as a horizontal distribution on a 10°×10° grid, as well as averages over specific regions providing both hemispheric-scale (with the exception of the North Pacific region) and regionally resolved information on midlatitude and subtropical to tropical UT ozone changes. Long-term differences are strongly dependent on region and can be summarised as follows:

- Over the western United States, long-term differences are small and statistically not significant.
- Over the northeastern United States, long-term differences are mostly positive. Largest increases are found in winter and still considerable increases are seen in spring. In summer and autumn, differences are much smaller and statistically not or only marginally significant.
- Over the Atlantic, a similar seasonal change pattern as over the northeastern United States is found with significant increases in winter and somewhat smaller increases in spring. No significant changes are seen in summer and autumn, possibly due to a strong bias of the GASP data toward the year 1978 when ozone concentrations were probably anomalously high.
- Over Europe, long-term differences are positive in all seasons except in autumn. There, differences may not be representative of a longer-term change as only three years of GASP data are available that are strongly biased toward the year 1978.
- Long-term differences over the Middle East indicate large increases in spring and summer. In autumn and winter, only moderate changes are identified. The spring and summer increases are probably related to anthropogenic ozone precursor emissions increases and associated photochemical ozone production over the Middle East and India regions. Surface ozone produced over India may reach

the UT through monsoonal convection and can be transported to the Middle East within the monsoonal anticyclonic circulation over South Asia.

- Over India, large significant increases are seen in spring and summer. Smaller and insignificant increases are found in autumn and winter. The large summer increase results in a changed seasonal cycle with the summertime minimum visible in the 1970s having disappeared in the 1990s. The change in seasonality may be due to drastic increases in ozone precursor emissions and an associated increase of tropospheric ozone over India over the last decades.
- Over Japan, no long-term changes could be derived for winter due to missing data availability. In all other seasons, mostly significant increases are found. Since local ozone precursor emissions have not substantially increased over the last two decades, but are rapidly increasing over China, a plausible cause for the increases may be Chinese NO_x emissions, associated ozone production, and advection to Japan.
- Over Southeast Asia, significant increases are seen in spring and summer. Besides increases in anthropogenic NO_x emissions, biomass burning must be considered a major contributor to changes in tropical ozone as large amounts of ozone precursors are released through it.

To analyse long-term changes in the LS, differences between the GASP and MOZAIC climatologies were calculated as function of EL and potential temperature distance from the tropopause. Statistically significant decreases are mostly found at midlatitudes in winter and spring in agreement with the downward trend between the 1970s and 1990s due to ozone depletion by halocarbons and the fact that downward transport of stratospheric ozone to the lowermost stratosphere is strongest in these seasons. In summer, representativeness of the GASP climatology may be limited and consequently, differences may not be indicative of a long-term change. In autumn at midlatitudes, small but statistically insignificant increases are found in the lowermost stratosphere. At higher altitudes above the tropopause and higher latitudes, significant decreases are found.

Long-term differences deduced from GASP/ MOZAIC were compared with respective changes derived from ozonesondes of the three European stations Uccle, MOHp, and Payerne, as well as of the US American station Wallops Island. In the UT, regionally averaged profiles of aircraft data were compared to respective sounding data. In the LS, the comparison was carried out in the EL/potential temperature framework. The results of the comparison sum up as follows:

- The early 1970s European BM sonde data agree with GASP within the range of uncertainty (UT) or measure slightly less ozone (LS). In contrast, the more recent sensors show consistently higher ozone values than MOZAIC both in the UT and LS. The unequal behavior in the 1970s and 1990s is associated with differing long-term changes: while the comparison between GASP and MOZAIC indicates changes of −5% to 10% over Europe, the BM sondes suggest a much larger increase of 10%–35% depending on station and season, although small sample sizes mostly prevent statistically significant conclusions.

- The comparison of UT ozone over the eastern United States derived from GASP/MOZAIC and from Wallops Island, where an ECC sensor has been in operation since the beginning of measurements, shows that the sonde measured more ozone than the aircraft data both in the 1970s and 1990s with indications that differences may be slightly smaller in the 1990s. A plausible cause for the reduced differences may be the reduction in the strength of the sensing solution of the sonde from 1.5% KI-buffer to 1% KI-buffer, accomplished in 1994, which is known to lead to reduced ozone mixing ratios. Consequently, long-term changes derived from aircraft are within the (relatively large) range of uncertainty or slightly larger than deduced from the sonde. Thus, our results may indicate that long-term changes derived from Wallops Island station data, that include periods of differing sensing solution strengths, may be underestimated by a few percent.

- Comparing the GASP aircraft with BM and ECC ozonesonde data over Europe and the USA, respectively, our results agree with earlier studies stating that early BM instruments measured less ozone than ECC sensors. The order of magnitude of differences indicated to be 10–25% in the literature is confirmed by this study.

- Acknowledging uncertainties due to sample size restrictions of aircraft and ozonesonde data especially in the 1970s, restricted precision of BM sondes, and methodology of our analysis, there are hints that the sensitivity of BM sensors to ozone in the UT/LS was different in the 1970s and 1990s resulting in long-term changes that may be considerably overestimated by the sondes. This applies to all BM series, and particularly to the Payerne station. While the behaviour of the early BM sondes appears to be in agreement with laboratory investigations, the positive bias of the 1990s BM sensors from MOZAIC remains unexplained. Not applying the CF, differences between sonde and MOZAIC measurements are decreased by a few percent, but a systematic offset remains. Considering the common use of both MOZAIC and BM sonde data for deriving long(er)-term trends, improved understanding of this discrepancy would be very desirable. To achieve the latter, further laboratory and field intercomparisons of ozonesondes vs. UV photometer, as well as coordinated activities to obtain measurements from simultaneous flights by MOZAIC and other aircraft would be highly recommendable.

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Table 1. Ozone sounding stations, total number of ascents during 03/1975–06/1979 and 08/1994–12/2001, number of ascents used in the study according to CF criterion (see text), and sensor type used. (*) Uccle ozone data available on WOUDC server are homogenised.

	Uccle	Payerne	MOHp	Wallops Island
Country	Belgium	Switzerland	Germany	USA
Lat (°)	50.8	46.49	47.8	37.93
Lon(°)	4.35	6.57	11.02	–75.48
Sensor	BM/ECC (*)	BM	BM	ECC
Total number 1970s (N_{70s})	572	516	345	149
Number used 1970s (% of N_{70s})	73	90	93	94
Total number 1990s (N_{90s})	1078	1162	900	422
Number used 1990s (% of N_{90s})	90	90	98	74

Table 2. Mean relative LS ozone differences between sondes and aircraft for the GASP and MOZAIC periods (sonde-aircraft, %), and averaged long-term changes by sondes (1990s–1970s, %/decade). Averages over 10–60 K and 40–80° N EL, cf. Figs. 11–13. “sigma” denotes standard deviations over boxes. Fraction of boxes where differences are positive are also given.

		DJF	MAM	JJA	SON
1975–1979		Uccle			
	mean±sigma (%)	−2±10	−1±8	−8±13	−12±9
	fraction boxes: $\Delta O_3 > 0$ (%)	46	36	25	6
		MOHp			
	mean±sigma (%)	−4±12	−5±8	−12±9	−13±12
	fraction boxes: $\Delta O_3 > 0$ (%)	35	12	8	20
		Payerne			
	mean±sigma (%)	2±10	−4±10	−9±10	−2±11
	fraction boxes: $\Delta O_3 > 0$ (%)	58	22	14	40
1994–2001		Uccle			
	mean±sigma (%)	8±8	4±5	4±9	8±7
	fraction boxes: $\Delta O_3 > 0$ (%)	92	78	68	91
		MOHp			
	mean±sigma (%)	16±12	8±8	6±12	14±8
	fraction boxes: $\Delta O_3 > 0$ (%)	91	81	75	100
		Payerne			
	mean±sigma (%)	19±12	11±5	11±7	17±8
	fraction boxes: $\Delta O_3 > 0$ (%)	94	97	91	100
1990s–1970s		MOZAIC – GASP (cf. Fig. 7)			
	mean±sigma (%/)	−5±3	−3±4	−3±4	−1±4
	fraction boxes: $\Delta O_3 > 0$ (%)	6	21	19	50
		Uccle			
	mean±sigma (%)	7±10	4±9	7±14	23±16
	fraction boxes: $\Delta O_3 > 0$ (%)	76	74	67	100
		MOHp			
	mean±sigma (%)	17±17	13±14	11±13	39±14
	fraction boxes: $\Delta O_3 > 0$ (%)	88	88	77	100
		Payerne			
	mean±sigma (%)	14±12	15±10	15±11	24±12
	fraction boxes: $\Delta O_3 > 0$ (%)	87	93	93	95

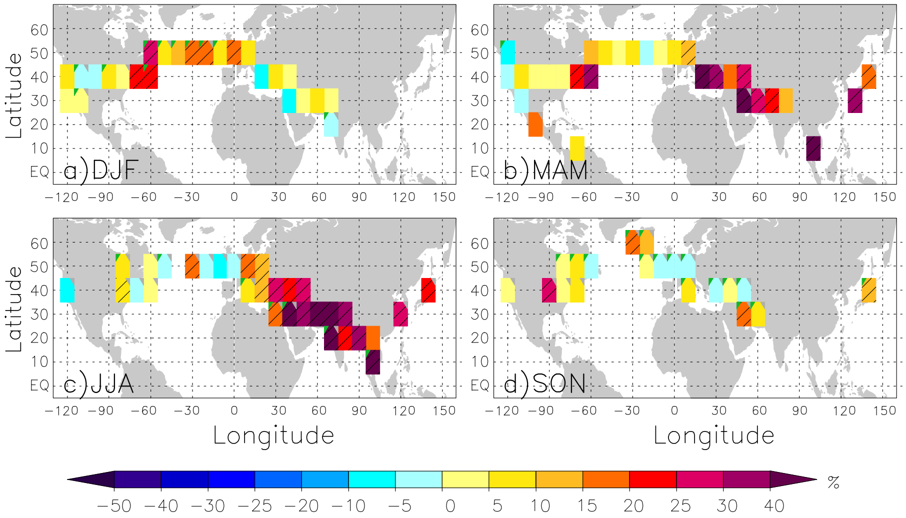

Fig. 1. Relative differences between GASP and MOZAIC UT ozone (MOZAIC-GASP/GASP) (in %) as function of latitude and longitude. Data have been averaged over a 10°×10° grid. Data were identified tropospheric using the 2 PVU tropopause in the extratropics and the thermal tropopause in the tropics (latitudes <35° N). Hatched boxes indicate where differences are statistically significant at the 95% level, grey triangles where GASP data are biased toward one year (≥50% from one year), and green triangles where GASP data are available from three years only. Differences have only been displayed where data from at least three years are available for the GASP period and number of daily means available for averaging is larger equal ten. **(a)** DJF, **(b)** MAM, **(c)** JJA, and **(d)** SON.

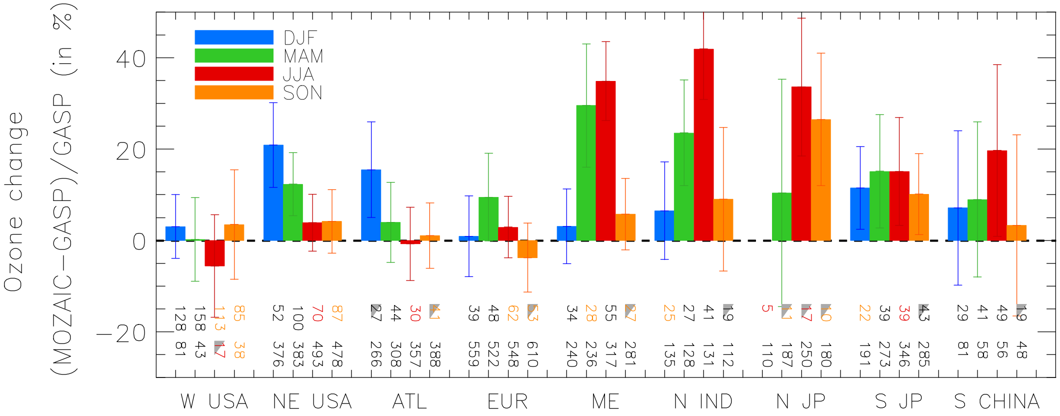

Fig. 2. Long-term changes of UT ozone between GASP and MOZAIC periods (MOZAIC-GASP/GASP) (in %) as function of season for the W USA, NE USA, ATL, EUR, ME, N IND, N JP, S JP, S CHINA regions (specifications of regions cf. SP2007, their Table 3. ME region is specified in the text). DJF: blue bars, MAM: green bars, JJA: red bars, and SON: orange bars. Relative differences have only been displayed if greater equal 10 daily regional averages are available for both GASP and MOZAIC periods. Vertical bars indicate 95% confidence intervals of differences. Bottom rows of numbers represent numbers of daily means available for averaging. Upper row: GASP, lower row: MOZAIC. Numbers are coloured in orange (red) if GASP or MOZAIC data are biased toward one year: 50–75% of data from one year (>75% from one year). Grey triangles mark regional averages for which data from three years only are available for averaging.

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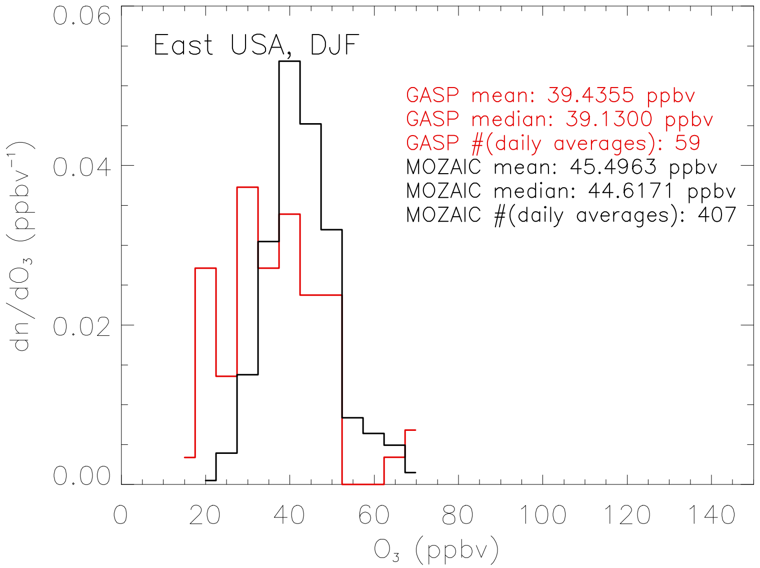

Fig. 3. Probability density function of UT ozone concentrations for the East USA region and DJF. The figure shows the GASP (red) and MOZAIC (black) distributions. Additionally, mean, median, and the ensemble size (i.e., number of daily regional averages) for building climatological means over the region are indicated.

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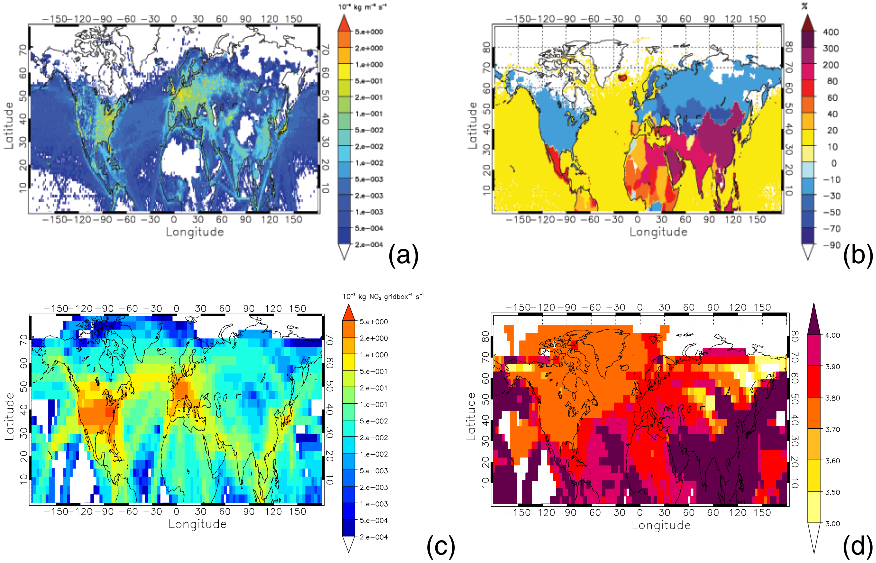

Fig. 4. **(a)** RETRO anthropogenic surface NO_x emissions for the period 1975–1979 (10^{-9} kg m^{-2} s^{-1}), **(b)** relative difference between periods 1975–1979 and 1994–2000 (1994–2000–1975–79) (%). Sources included are power generation, industrial, residential, and commercial combustion, transport, and ships (Schultz, 2007). The positive differences in NO_x emissions change over the oceans are due to a uniform global scaling factor applied to derive historical ship emissions. For the comparison of 1975–1979 and 1994–2000, the factor equals 1.1. **(c)** RETRO aircraft NO_x emissions at 10.5 km altitude for the period 1975–1979 (10^{-9} kg gridbox^{-1} s^{-1}), and **(d)** ratio of aircraft emissions 1994–2000/1975–1979. The emissions inventories are based on the DLR-1992 and DLR-2015 data sets interpolated according to IPCC (1999) using an exponential function between 1992 and 2015 (V. Grewe, personal communication, 2003). See also Schmitt and Brunner (1997).

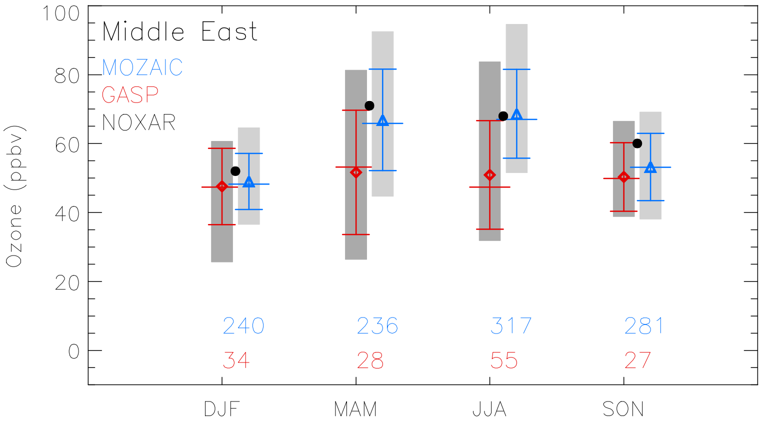

Fig. 5. Seasonal cycle of UT ozone above the Middle East (25–45° N, 30–60° E) for GASP (red), MOZAIC (blue), and NOXAR (black) climatologies (ppbv). NOXAR data have been processed in analogous way as GASP and MOZAIC and are representative of the years 1995/1996 (Brunner et al., 2001). Symbols denote arithmetic means, horizontal bars medians. Vertical bars show standard deviation, and grey vertical ranges central 90% of data. Numbers at the bottom indicate number of daily regional averages.

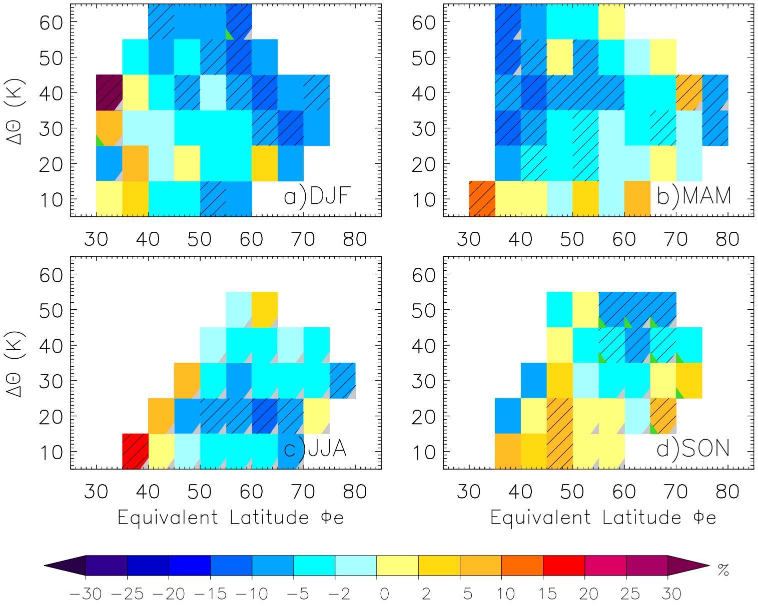

Fig. 6. Relative differences between GASP and MOZAIC quasi-zonal mean LS ozone (MOZAIC-GASP) (%) as function of equivalent latitude and potential temperature distance from the tropopause. Hatched boxes indicate where differences are statistically significant at the 95% level, grey triangles where GASP data are biased towards one year (≥50% from one year), and green triangles where GASP data are available from three years only. Differences have only been displayed where at least 30 daily means and data from at least three years are available for the GASP period. **(a)** DJF, **(b)** MAM, **(c)** JJA, and **(d)** SON.

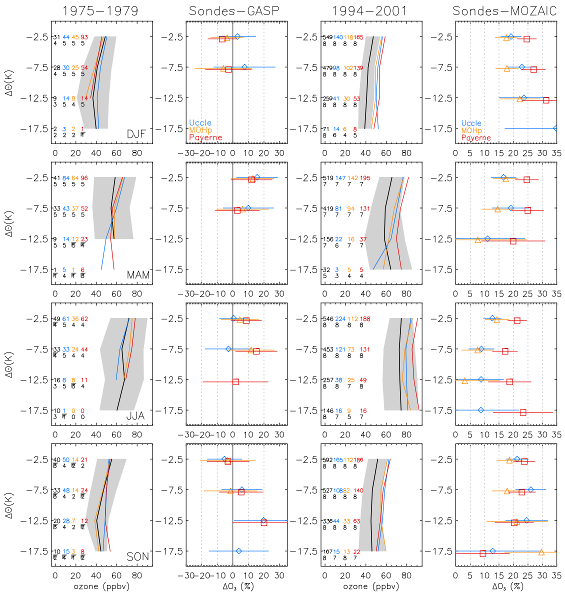

Fig. 7. GASP, MOZAIC, and balloon UT ozone (1975–1979) over Europe at potential temperature distance from the 2 PVU tropopause. GASP and MOZAIC data have been averaged over the EUR region (SP2007, their Table 3). Left column: GASP and sonde vertical profiles (ppbv), GASP data range within ±1σ (grey shading), number of daily means (black: GASP (daily averages over EUR region), blue: Uccle, orange: MOHp, red: Payerne), number of years where data are available (second row of numbers), and grey triangles as indication when more than 50% (70%) of data stem from one year of data when data from greater equal (less than) three years are available. Second column: Relative differences between GASP and balloon data (sondes-GASP, %). Horizontal bars: 95% confidence intervals of differences. Third column: as first column, but for MOZAIC period. Fourth column: as second column, but for MOZAIC period. Differences between aircraft and sonde data in second and fourth column have only been displayed if the number of daily averages is ≥10. First row DJF, second row MAM, third row JJA, and fourth row SON.

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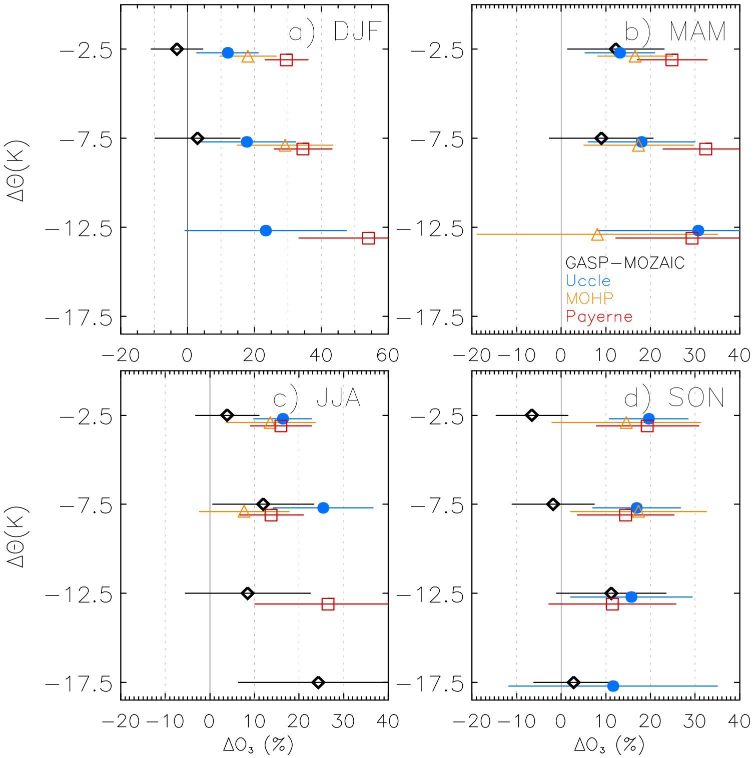

Fig. 8. Relative differences of climatological UT ozone profiles between 1975–1979 and 1994–2001 (%) (1990s–1970s) by aircraft and sonde data over Europe at potential temperature distance from the 2 PVU tropopause. GASP and MOZAIC have been averaged over the EUR region. Differences have only been displayed if number of daily averages is ≥10 for all data (cf. numbers in Fig. 7). Black: MOZAIC-GASP, blue: Uccle, orange: MOHp, and red: Payerne. Horizontal bars indicate 95% confidence intervals of differences. **(a)** DJF, **(b)** MAM, **(c)** JJA, and **(d)** SON.

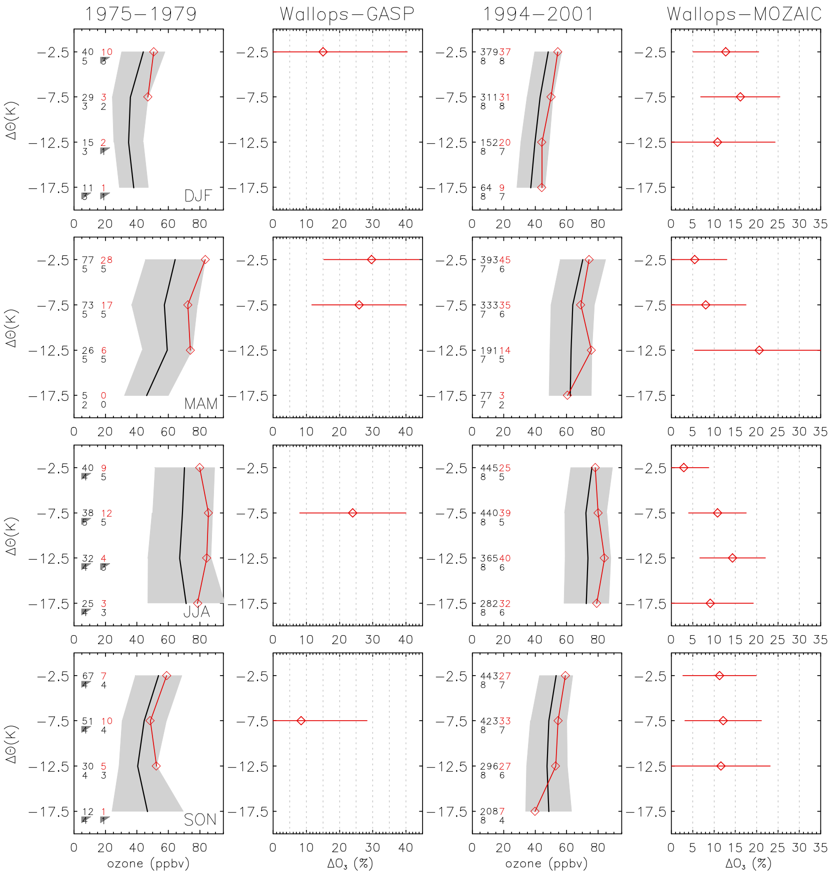

Fig. 9. As Fig. 7, but aircraft data averaged over East USA (90° W–60° W, 30° N–50° N) and Wallops Island sonde data. Differences between aircraft and sonde data have only been displayed if at least 10 daily averages were available.

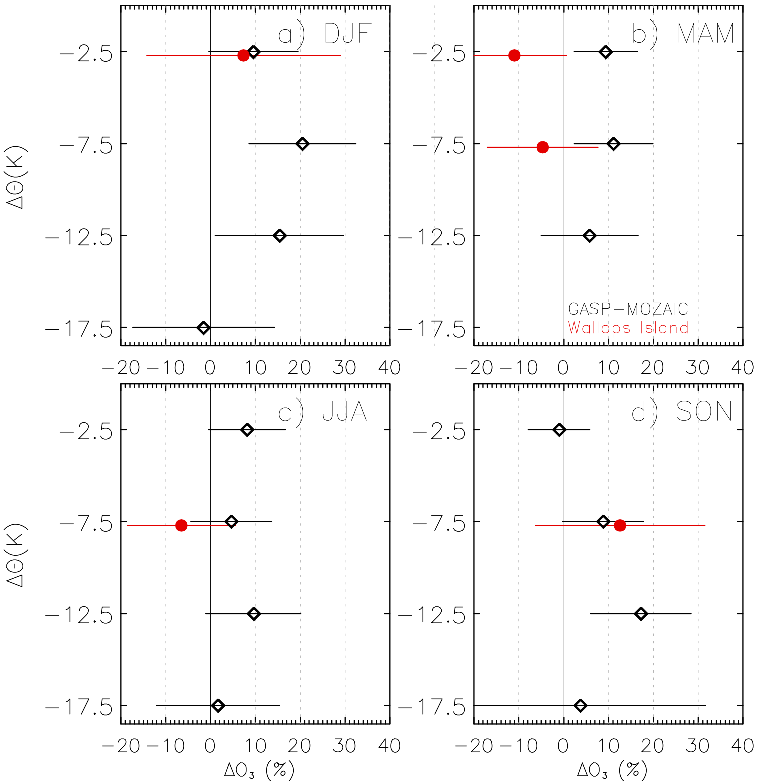

Fig. 10. As Fig. 8, but aircraft differences calculated for the East USA region (90° W–60° W, 30° N–50° N) (black diamonds) and sonde differences for Wallops Island station data. Differences are only displayed if greater equal ten daily means are available for both aircraft and sonde data at each level.

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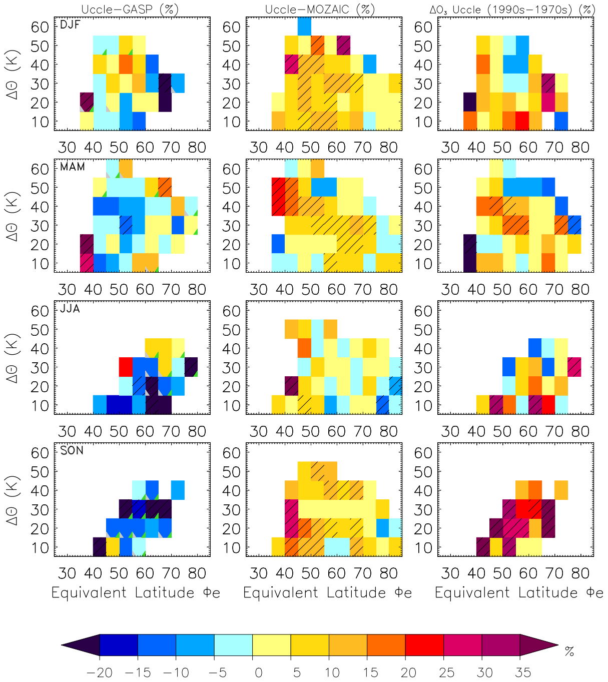

Fig. 11. Differences of LS ozone as function of potential temperature distance from the 2 PVU tropopause and equivalent latitude. Left column: Uccle-GASP (1975–1979) (%), middle column: Uccle-MOZAIC (1994–2001) (%), and right column: long-term changes of Uccle soundings deduced from 1970s and 1990s climatologies (1990s–1970s, %). Climatological averages have been calculated from daily means. Hatched boxes indicate where differences are statistically significant at the 95% level, grey triangles where Uccle 1970s data are biased towards one year (≥50% from one year), and green triangles where Uccle data are available from three years only. Differences have only been displayed where at least 5 daily means and data from at least three (six) years are available for the GASP (MOZAIC) period.

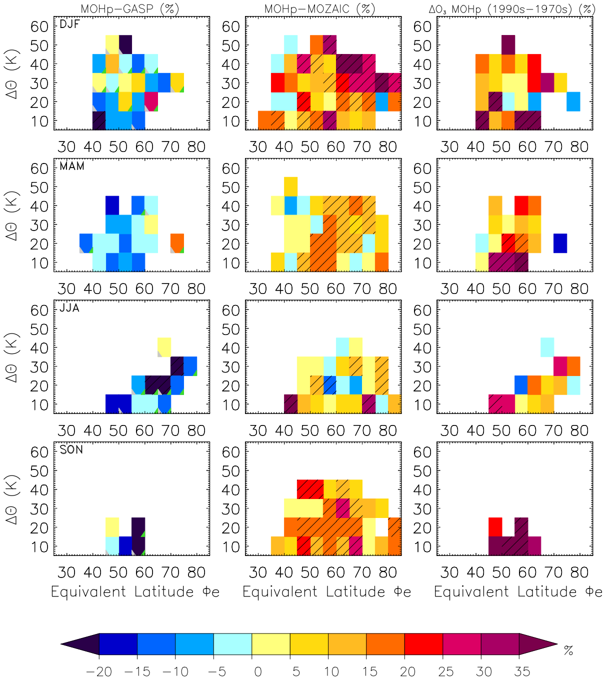

Fig. 12. As Fig. 11, but comparison of MOHp and aircraft data.

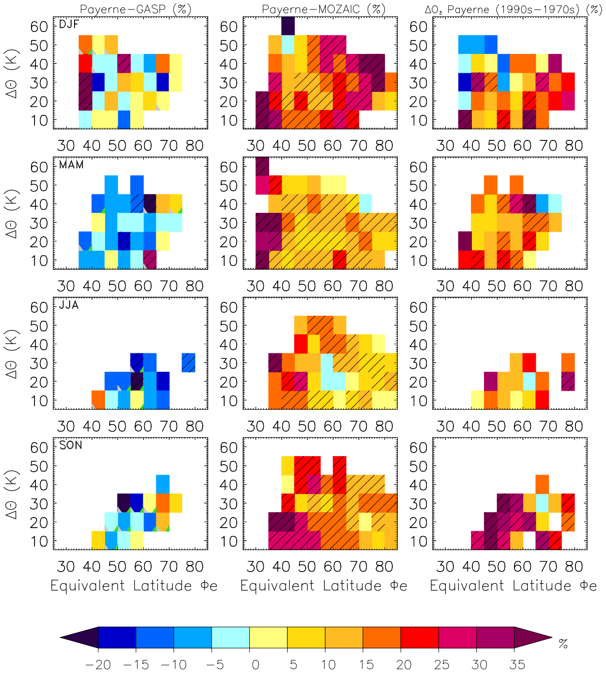

Fig. 13. As Fig. 11, but comparison of Payerne and aircraft data.