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Mid-latitude Tropospheric Ozone Columns from the MOZAIC program: climatology and interannual variability

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Abstract

Several thousands ozone vertical profiles collected in the course of the MOZAIC program (Measurements of Ozone, Water Vapour, Carbon Monoxide and Nitrogen Oxides by In-Service Airbus Aircraft) from August 1994 to February 2002 are investigated to bring out climatological and interannual variability aspects. The study is centred on the most frequently visited MOZAIC airports, i.e. Frankfurt (Germany), Paris (France), New York (USA) and the cluster of Tokyo, Nagoya and Osaka (Japan). The analysis focuses on the vertical integration of ozone from the ground to the dynamical tropopause and the vertical integration of stratospheric-origin ozone throughout the troposphere. The characteristics of the MOZAIC profiles, frequency of flights, accuracy, precision, and depth of the troposphere observed, are presented. The climatological analysis shows that the Tropospheric Ozone Column (TOC) seasonal cycle ranges from a minimum wintertime at all four stations to a spring-summer maximum in Frankfurt, Paris, and New York. Over Japan, the maximum occurs in spring because of the earlier springtime sun. The invasion of monsoon air masses in the boundary layer and in the mid-troposphere then steeply diminishes the summertime value. Boundary layer contributions to the TOC are 10% higher in New York compare to Frankfurt and Paris during spring and summer, and are 10% higher in Japan compare to New York, Frankfurt and Paris during autumn and early spring. Local and remote anthropogenic emissions as well as biomass burning over upstream regions of Asia may be responsible of larger low- and mid-tropospheric contributions to the tropospheric ozone column over Japan throughout the year except during the summer-monsoon season. A simple Lagrangian analysis has shown that a minimum range of 10% of the TOC is of stratospheric-origin throughout the year. The investigation on the short-term trends of the TOC over the period 1995–2001 shows a linear increase of 0.7%/year in Frankfurt, 0.8%/year in Japan, 0.9%/year in Paris, and 1.1%/year in New York. Essential ingredients to these positive short-term trends are the continuous increase of wintertime tropospheric ozone columns from 1996 to 1999 and the positive contributions of the

mid-troposphere whatever the season.

1. Introduction

Tropospheric ozone is a trace gas with a large natural variability in space and time and a mixing ratio in the range of about 10–100 ppbv. The origin of tropospheric ozone is either in-situ photochemical production or ozone flux transported from the stratosphere. Listed as a pollutant with regard to human health and plants, tropospheric ozone is a by-product of the photo-oxidation of hydrocarbons. For many years, photochemical air pollution was considered as a problem of mainly local or regional significance, somewhat affecting clean air sites by the advection of polluted urban plumes that spread over the countryside. It was discovered later on that smog-like reactions associated with the oxidation of methane and other hydrocarbons induce the photochemical production of ozone also in the unpolluted troposphere (Crutzen, 1973, 1974). The role of photochemistry in controlling the tropospheric ozone was therefore questioned (Chameides and Walker, 1973, 1976). The controversy that arose from proponents of a tropospheric ozone budget dominated by stratospheric-origin downward transport (Fabian, 1974; Chatfield and Harrison, 1976) was anchored in the incapability to clarify which of the stratospheric flux or the photochemical production may be responsible of the spring-summer lower tropospheric ozone maximum. The quantitative assessment of the cross-tropopause exchanges fluxes of mass, ozone and other chemical constituents is of major importance for atmospheric chemistry and climate. Regener (1957) and Junge (1962) considered the stratosphere to be the main source from which ozone enters the troposphere via tropopause exchange processes. Ozone is transported from the lower stratosphere into the upper troposphere through tropopause folding (Danielsen et al., 1968, 1987) and exchanged with the troposphere via diabatic processes and turbulent diffusion (Lamarque and Hess, 1994), mixing processes and convective erosion during the breakup of stratospheric filaments (Appenzeller et al., 1996; Gouget et al., 2000). Climatological global-scale studies based

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on trajectory calculations and operational analysis data have been developed in the last years. The principle is to identify exchange events with the time traces of potential vorticity along a large set of trajectories. Wernli and Bourqui (2002) introduce a residence time criterion that serves to distinguish transient and irreversible exchange events, the former only influencing the layers near the tropopause, the latter having the potential to contribute to the tropospheric ozone budget. Applied on one year of operational analyses, the methodology shows that the seasonal cycle of the hemispherically integrated net exchange mass flux is downwards in the extratropics with a maximum (minimum) in winter-spring (autumn). In contrast to the net exchange, previous authors identify a symmetric two-way exchange that has almost no seasonal variation and a larger amplitude than the net exchange, and is strongly sensitive to the residence time. In conclusion of recent Lagrangian studies, Stohl et al. (2003) insist on the importance of separating deep stratosphere-troposphere transport from shallow stratosphere-troposphere transport, the former stream contributing to 5% of the tropospheric mass when the residence time criterion is 4 days. Deep stratosphere-troposphere transport has a winter maximum mainly near the Atlantic and Pacific storm track entrance and exit regions, which is, according to the previous authors, an indication that they are not the cause of the late springtime maximum of ozone in the lower troposphere. Shallow stratosphere-troposphere transport has a weak amplitude seasonal cycle. With regard to long-lasting ozone measurements in Europe, it was found that the concentration of ozone has been increased not only in the air near the Earth's surface (Feister and Warmbt, 1987; Volz and Klein, 1998), but also in the free troposphere (Staehelin and Schmid, 1991; Staehelin et al., 1994; Marenco et al., 1994). These results have been taken as an evidence for an increase in the photochemical production of ozone in the atmosphere due to the growing emissions of ozone precursors. In the troposphere over Europe, longest data time series with ozonesondes began in the 1960s at Hohenpeissenberg (Germany) and Payerne (Switzerland). Statistical studies for tropospheric long-term trends applied on this dataset have shown a large increase of tropospheric ozone (in the range of 0.7–1.4%/year) since the beginning of the 1970s (Logan, 1985; Tia et al., 1986; Staehelin and Schmid, 1991; Harris et al., 1997; Oltmans et al., 1998; Logan, 1994; Weiss et al., 2001). With regard to the UTLS region, Tarasick et al. (2005) compare overall linear trends for the 1980–2001 and 1991–2001 periods with Canadian ozonesondes data and show that negative trends for the former period have rebounded to positive trends in the latter period at all levels below 63 hPa without changes in tropopause height.

Therefore, the global distribution and trends of ozone in the troposphere remains a major focus of interest. Comprehensive and continuous observations are needed to contribute to the assessment of its role in the climate change. A major impediment to make progress on the previous issues is related to the deficiencies in the network of tropospheric ozone observations. Balloon-sounding stations are sparse and operate weekly. Research aircraft provide limited datasets in process-oriented experiments. The first faltering steps of satellite retrieval techniques in the upper troposphere and lower stratosphere (UTLS) domain are still not quantitative enough. One of the largest ozone databases existing today comes from the MOZAIC program (Measurements of Ozone, Water Vapor, Carbon Monoxide and Nitrogen Oxides by In-service Airbus Aircraft, Marenco et al., 1998, http://www.aero.obs-mip.fr/mozaic/). Using automatic equipment installed on board five long-range Airbus A340 aircraft flying regularly all over the world, about 46 000 vertical profiles of ozone between 0 and 9–12 km altitude and about 23 000 time series along inter-continental flight routes have been acquired since 1994. The initial ozone climatology produced in the UTLS domain with the first two years of MOZAIC measurements (Thouret et al., 1998a) compared well to data from the ozone sounding network (Thouret et al., 1998b). A new UTLS ozone climatology, based on the 1994–2003 MOZAIC measurements and referenced to the altitude of the dynamical tropopause, is being described in a companion study (Thouret et al., 2005).

The general aim of this work is to better document the spatial and temporal distribution of tropospheric ozone and its variability in the mid-northern latitudes from a MOZAIC sub-dataset of vertical profiles at the few most frequently visited airports. The study is orientated towards the seasonal and inter-annual analysis of two vertically integrated quantities, the tropospheric ozone column which is the integrated ozone profile through the depth of the troposphere, and the stratospheric intrusion ozone column which is the integrated stratospheric-origin ozone profile through the depth of the troposphere. A Lagrangian methodology is used to discriminate stratospheric- and tropospheric-origin ozone below the tropopause. Motivations to study vertically integrated quantities are: i) to deliver an integrated view of the ozone column in the troposphere, ii) to make meaningful comparisons of ozone columns in the boundary layer, in the mid-troposphere, and in the upper-troposphere, iii) to compare the impact of stratosphere-troposphere exchange versus photochemical sources, iv) to provide meaningful comparisons with present and future satellite retrieval techniques that provide the tropospheric ozone column, v) to provide models with seasonal-mean and regional-mean data for initialisation. The present MOZAIC dataset allows a limited investigation of the interannual variability of the tropospheric ozone column as well as an assessment of its trends in the short-term (the 7-years period from January 1995 to December 2001 investigated here). From now on, in order to shorten, trends in the short-term will be noted trends as far as MOZAIC dataset is concerned. The aim is to quantify the Tropospheric Ozone Column (TOC) at mid-northern latitudes, to give an assessment of the contribution of stratospheric-origin air to TOC, and to investigate the interannual variability and the trends of TOC. Section 2 presents the MOZAIC data, Sect. 3 is devoted to definitions and methodology, Sect. 4 is a climatology of TOC, Sect. 5 investigates the trends and the interannual variability of TOC. Finally, we summarize our main results in section 6.

2. MOZAIC data

Measurements of ozone in the MOZAIC program are taken every four seconds from take-off to landing. Based on the dual-beam UV absorption principle (Model 49–103 from Thermo Environment Instruments, USA), the ozone measurement accuracy is estimated at ± [2 ppbv+2%] (Thouret et al., 1998a). From the beginning of the program in 1994, the measurement quality control procedures have remained unchanged to ensure that long-term series are free of instrumental artefact. Instruments are laboratory calibrated before and after the flight periods, the duration of which is generally 12 to 18 months. The laboratory calibration is performed with a reference analyser which is periodically cross-checked with a National Institute of Standards and Technology in France. Additionally and during the flight operation period, each instrument is regularly checked for the zero and for the calibration factor, using a built-in ozone generator. Furthermore, intercomparisons are made between aircraft when they fly close in location and time, which happens several times a month. In this study, measurements used are ascent and descent profiles from August 1994 to February 2002. Raw data (4 s time resolution) are averaged over 150 m height intervals. To help the interpretations of MOZAIC data, meteorological parameters derived from operational European Centre for Medium-Range Weather Forecast (ECMWF) analyses and interpolated along aircraft trajectories have been added by Météo-France in the MOZAIC database, like pressure levels of four Potential Vorticity (*PV*) values (1, 2, 3 and 4 pvu), the *PV* itself and a reconstructed potential vorticity *RPV* with a Lagrangian method. Details are given in the following section. Table 1 list all abbreviations used in the paper.

A subset of mid-latitude MOZAIC sites, having high frequencies of observations and spread over the northern hemisphere, has been selected. It is made up of Frankfurt (Germany) with 6338 vertical profiles (operation of two aircraft from this airport), Paris (France) with 3308 vertical profiles, New York (USA) with 2631 vertical profiles, and of the cluster of Tokyo, Nagoya and Osaka (Japan) with 1899 vertical profiles. Frankfurt and Paris, 650 km apart, will be used as a subset to assess the mesoscale variability of the results. The closeness of the three Japanese cities visited by MOZAIC is turned to good account to constitute one MOZAIC site with a suitable regional sampling frequency for Japan. Profiles are defined as the part of the flight between ground level and the first pressure stabilized cruising level, usually up to about 300 hPa (200 hPa) with regard to the ascent (descent) profile. Tracks of aircraft profiles at the ground display a disk of about 400 km radius in Frankfurt and Paris, a quarter of disk facing northeast in New York, and half of a disk facing northwest over Japan. We consider aircraft profiles as valuable as balloon soundings to compute tropospheric ozone columns in spite of the atmospheric volumes delimited by the ground tracks of aircraft vertical profiles, somewhat larger than the ones of balloon soundings, and the larger ascent rates of balloon soundings. These discrepancies were evaluated by Thouret et al. (1998b).

Monthly time series of flight numbers over the 4 MOZAIC sites are displayed on Fig. 1. Frankfurt has the best sampling frequency with an average of 70 profiles per month and minimum monthly numbers exceeding 30 except in August 1994 and March 2001. Paris has a good sampling frequency with an average of 36 profiles per month with nevertheless 2 profiles per month in September 1995, and some periods with none in March 1998, December–January 2000 and May 2001–January 2002. An average of 30 profiles per month is reached in New York with less than 10 profiles per month in December 1998–March 1999 and in January–February 2002. Japan has an average of 20 profiles per month with less than 5 profiles per month during August 1994–March 1995 and February 2002. Note that the measurement frequency for most of the ozone sonde stations of the northern hemisphere is weekly (WOUDC web site: http://www.woudc.org/data_f.html).

3. Definitions and methodology

3.1. Tropospheric ozone column

Several tropopause definitions exist. The thermal tropopause is defined by WMO (1957) as the lowest level where the temperature lapse rate falls below $\Delta T/\Delta Z$=2 K/km and its average between this level and all higher levels within ΔZ=2 km remains below this value. The dynamical tropopause is defined with a threshold on the potential vorticity (Ertel, 1942). The *PV* threshold for the dynamical tropopause ranges from 1.0 pvu (Bithell et al., 2000; Hoskins et al., 1985) to 3.5 pvu (Hoerling et al., 1991;

Hoinka, 1998). A chemical tropopause has been defined by Bethan et al. (1996) with criteria on vertical gradients of ozone mixing ratio. In the present study, we use the dynamical tropopause (*DT*) defined with a 2.0 pvu *PV* threshold (Thouret et al., 2005). Coming down from the top of the aircraft profile, *DT* is defined at the first intersection with the 2 pvu *PV* threshold. We further arbitrarily consider three vertical layers in the depth of the troposphere. The layer from the dynamical tropopause to 8 km altitude refers to the upper-troposphere (*UT*). The 8–2 km altitude layer refers to the mid-troposphere (*MT*). The 2–0 km altitude layer refers to the boundary layer (*BL*).

Tropospheric Ozone Columns (*TOC*) are calculated from the ground to the dynamical tropopause (Fig. 2). *TOC*, expressed in Dobson Units (*DU*), is the equivalent thickness of ozone contained in the tropospheric vertical column of one cm^{-2} section compressed down to standard temperature and pressure such that 10^{-5} m corresponds to 1 DU which is $2{,}6861020 \cdot 10^{16} \cdot mol \cdot cm^{-2}$ (Andrews et al., 1987). The contribution to *TOC* of a basic atmospheric layer of 150-m vertical depth is called Ozone Layer Thickness (*OLT*), so that *TOC* is the integration of *OLT* from ground to *DT*, while the integration of *OLT* from ground to the top of the MOZAIC vertical profile is called *MOC* for MOZAIC Ozone Column. The detailed computation of *OLT* is given in the Appendix.

Stratospheric intrusions into the troposphere occur during tropopause folding in narrow regions near upper-tropospheric fronts (Danielsen, 1968) and can be traced by characteristic features like high static stability, high ozone content, low water vapor content, and high potential vorticity. In presence of a tropopause fold, e.g. when the 2 pvu contour folds below the tropopause (see Fig. 2), stratospheric-origin ozone is included in the *TOC* like we have defined it. *TOC* may be dramatically increased with stratospheric-origin intrusions because ozone observations across tropopause folds often show high ozone concentrations. For instance, Danielsen et al. (1987) and Browell et al. (1987) reported mixing ratio of ozone in excess of 200 ppbv in a 2.0-km-deep tropopause fold observed with airborne lidar and in situ measurements in the upper troposphere. The contribution of stratospheric-origin ozone to *TOC* assessed using Eq. (6) (see Appendix) for a hypothetical tropopause fold of 1.5-km depth with a

150-ppbv homogeneous ozone mixing ratio at 400 hPa and −20°C is about 10 DU (or equivalently 1 DU/150 m on the vertical), which may represent up to 50% (25%) of the monthly-mean *TOC* observed at mid-latitudes during winter (summer) as described in following sections. Stratosphere-troposphere exchanges may therefore be a more or less important contributor to the tropospheric ozone budget according to whether intrusions are deep, transient or shallow when penetrating into the troposphere (Wernli and Bourqui, 2002; Stohl et al., 2003). The identification of the stratospheric origin of air parcels with thermodynamical parameters may be achieved through Lagrangian approaches (Wernli and Davies, 1997; Stohl, 2001). Here, the Lagrangian parameter used, the Reconstructed Potential Vorticity (*RPV*), is the *PV* value at the end of a 24-h backward air parcel trajectory initialised at the location of the observation and computed with 6-hourly winds from ECMWF analyses. A recent stratospheric-origin (≤24 h) is allocated to an air parcel if a triple criteria is met: $RPV \geq 1.5$ pvu, altitude >2000 m and observed relative humidity (*RH*) <50%. The criterion on *RPV* is a compromise. It has to be less than the one for the dynamical tropopause in order to take into account non-conservation effects in trajectories and the numerical diffusion by the parent model. It has to be large enough to avoid capturing tropospheric-origin air parcels with *PV* diabatically enhanced in a region of strong latent heat release. The second criterion on the altitude prevents to capture air parcels with a relatively large *PV* enhanced by a thermal inversion at the top of the Boundary Layer. At last, the dryness criterion on the relative humidity is to strengthen the characteristics of stratospheric-origin air. No criterion is imposed on the ozone observation as it will be used to test the confidence in the method. With this method and as illustrated on Fig. 2, we define two new quantities. The Stratospheric Intrusion Column *SIC* is the integrated ozone profile through layers that fulfil stratospheric-origin ozone criteria ($RPV > 1.5$ pvu, z>2000 m, RH≤50%) below the dynamical tropopause. The Pure Tropospheric Ozone Column *PTOC* is the difference between *TOC* and *SIC*.

In order to illustrate the computation of *TOC*, *SIC* and *PTOC* quantities, four individual MOZAIC profiles over Frankfurt are illustrated on Fig. 3. The first vertical profile

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(Fig. 3a) presents typical signatures of the tropopause, like the change in the temperature lapse rate, the dryness, and the well defined vertical gradient of ozone mixing ratio. The dynamical tropopause *DT* is given at 7850 m altitude with the *PV* threshold which is correct with regard to the temperature lapse rate but may be a little bit too high with regard to the ozone mixing ratio. As a consequence, the rapid increase of the *OLT* profile from 0.6 to 0.8 DU/150 m just below the tropopause is counted as a contribution to *TOC* which is uncertain but has nevertheless a minor impact. *TOC* is about 21 DU and there is no stratospheric-origin contribution in it as the *RPV* profile never exceeds the 1.5 pvu threshold. The second vertical profile (Fig. 3b) also presents clear tropopause signatures in the observations in coherence with the dynamical tropopause given at 10 028 m. The *RPV* threshold method detects a typical stratospheric-origin layer in the mid-troposphere between 5812 m and 6679 m where ozone is anti-correlated with the relative humidity, and the lapse rate temperature is decreasing. In this layer the ozone mixing ratio is larger than 100 ppbv, or equivalently *OLT* is larger than 0.8 DU/150 m. The contribution of *SIC* to *TOC* is 5.93 DU, about 18% of *TOC*. On the third vertical profile (Fig. 3c) the dynamical tropopause is defined and crossed at 9828 m. Data show a characteristic tropopause fold around 4700 m, with a 90 ppbv ozone peak, 10% minimum relative humidity and *OLT* maximum close to 0.8 DU/150 m. The case study was used by Nédélec et al. (2003) in a validation paper for ozone and carbon monoxide measurements from the MOZAIC program. However, this tropopause fold is not detected by the *RPV* threshold method, and so does not contribute to *SIC* though it does for *TOC*. It shows that improvements of the Lagrangian approach would certainly be needed to capture all stratospheric intrusions. Below the tropopause there are some layers where *RPV* exceeds its 1.5-pvu threshold, however these layers are considered of tropospheric-origin because humidity is very high. In the last example (Fig. 3d) the dynamical tropopause is defined at 11 000 m and is not crossed by the aircraft that stops climbing at about 9 km altitude. The vertical profile of *OLT* (in DU/150 m) has been filled up from 9128 m till the level of the dynamical tropopause with a method described in the next section. In the planetary boundary layer, ozone pollution is visible

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with a 80 ppbv maximum at 1000 m, *OLT* values exceed 1.2 DU/150 m and strongly contribute to *TOC* which is close to 40 DU. To summarise, *TOC* values of the previous MOZAIC profiles are between 23 and 40 DU. The maximum *OLT* contribution to *TOC* can be either located in the boundary layer, the mid-troposphere or the upper-troposphere. A given ozone mixing ratio will obviously contribute more to *TOC* in the lower-troposphere than at any other higher level in the troposphere, because of greater air density at lower heights (Eq. 6 in the Appendix).

3.2. Missing data in vertical profiles

Missing data in tropospheric profiles occur for two reasons. First, there are data gaps that are due to the operation of the MOZAIC ozone analyser (internal calibration periods, resets, powercuts,...). With regard to this, data gaps take up one or several 150-m deep layers with a frequency that does not exceed 5% of the data set used in this study. If data is missing for just one *OLT* (i.e., a 150-m deep layer; see Fig. 2) in a profile, then the missing value is computed using a linear interpolation between data of the two nearest layers in the same profile. If data for more than one *OLT* are missing (i.e. a gap exceeding 150-m depth), each missing *OLT* value is replaced by its seasonal climatological value computed using the MOZAIC dataset (see Sect. 4.1). Second, there are the MOZAIC profiles that do not reach the dynamical tropopause. Here, our strategy is to fill up the unexplored atmospheric layers as high as possible by replacing missing *OLT* values with their corresponding seasonal climatological values. If the dynamical tropopause for a given flight is situated above the top of the seasonal climatological profile (about 12 km altitude in practice for MOZAIC aircraft), the profile is filled up to the latter level and we decide not to fill up the unexplored remainder. The contribution to *TOC* of the unexplored remainder of the profile is all the more important since the tropopause is high, with nevertheless a balancing effect due to the dependency of *OLT* to pressure. Impacts of the filling-up process and unexplored remainders of profiles are evaluated and discussed below.

On an annual-mean basis the dynamical tropopause is crossed for 44.4% of the

MOZAIC vertical profiles in Frankfurt, 39.5% in Paris, 33.5% in New York and 19.0% over Japan (see column P1 in Table 2). Filling-up vertical profiles with seasonal climatological *OLT* values when the tropopause of the day is higher than the top of the aircraft profile occurs for 47.6% of the profiles in Frankfurt, for 50.2% in Paris, for 38.2% in New York, and for 25.3% over Japan (column P2). Some vertical profiles are still uncompleted after this step because the *PV* profiles are not available on the data base, which occurs for less than 2% of the profiles whatever the site (column P3). Finally, there are other uncompleted profiles because the tropopause of the day is higher than the maximum altitude of the seasonal climatological profile, which ranges from 6.5% over Frankfurt to 54.5% over Japan (column P4). We choose to only discard P3 profiles from this study. Discarding all incomplete profiles (P2 and P4 columns) would bias the study towards systematic lower tropopause situations and eliminate about 80% of the Japanese profiles for the study of the mid-troposphere and the boundary layer. Keeping these profiles avoid the aforementioned bias. However their filling-up process weights the assessment of the short-term tendency of *TOC* with the contribution of a fixed seasonal value, and there is an underestimation of *TOC* for P4 profiles. These effects, that may become important in New York and Japan during summertime when the tropopause is the highest, are now assessed.

Monthly mean pressure of the dynamical tropopause for the 4 MOZAIC sites is shown on Fig. 4. Blue lines are when applying the tropopause detection method with the *PV* threshold on ECMWF analyses at the sampling frequency of MOZAIC flights (Column P in Table 2). A marked low (high) tropopause is visible in winter (summer) over New York and over Japan, whereas the seasonal variations of tropopause pressure over Frankfurt and Paris have a somewhat flat seasonal cycle. Differences are mainly due to the position of the sites with regard to main storm-tracks, in the entrance region of Atlantic (Pacific) storm-tracks for New York (Japan), and in the exit region of the Atlantic storm-tracks for Frankfurt and Paris. Black lines show monthly mean pressure of the dynamical tropopause when it is crossed by MOZAIC aircraft (Column P1 in Table 2), and red lines show monthly mean pressure after the filling-up process

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on vertical profiles (Columns P1 plus P3 in Table 2). For a given station, the difference between black and red lines is therefore a measure of the efficiency of the method used to fill up the vertical profiles (the more distant the lines, the more effective the method), and the difference between red and blue lines is a measure of the depth of unexplored remainders below the tropopause (the more distant the lines, the thicker the layer). Over Frankfurt, and Paris, the mean depth of unexplored remainders is very thin (≃10 hPa) and constant throughout the year. Over New York, it is quite thin in winter and spring but it increases to about 20–30 hPa from June to September. Over Japan the maximum depth of unexplored remainders is about 60 hPa during summer. Summertime *TOC* over New York and over Japan analysed in Sect. 4 are therefore underestimated because of the non-negligible depth of unexplored remainders below the tropopause. Based on a mean value for *OLT* of 0.3 DU/150 m (see Sect. 4, the maximum summertime losses in unexplored remainders are estimated to be about 0.3 DU over Frankfurt, 3 DU over New York and 5 DU over Japan. The monthly-mean contribution to *TOC* by the filling-up process is shown on Fig. 5. This contribution corresponds to the integrated ozone profile through the part of the upper troposphere which is bordered by the red and blue lines of Fig. 4 and that has been filled up with the corresponding part of the seasonal climatological profile. During summer it ranges from 2.8 DU at Frankfurt to 4.7 DU over Japan, while this contribution is about to 2 DU for all sites during winter. It is assessed to be about 10% of *TOC* whatever the season and the site. It is clear that the filling-up process improves the quantitative assessment of *TOC*. However, it has also an impact on the investigation of short-term trends by introducing a constant in the dataset.

4. Climatological analysis

4.1. Vertical profiles

Seasonal climatological vertical profiles of *OLT* are plotted on Fig. 6. The vertical gradient of *OLT* is positive in the boundary layer whatever the season and the site, and becomes negative in the free troposphere. Then, a distinction is made whether the seasonal-mean is computed with all profiles (thin lines) or with sections of the profiles below the dynamical tropopause (thick lines). With all profiles, the large stratospheric ozone concentrations make the vertical gradient of *OLT* to return to positive values in the upper part of the profile (Fig. 6, thin lines). The range of altitude where the vertical gradient of *OLT* changes its sign is nearby the seasonal-mean tropopause, i.e. between 8 and 10 km on every station and for every season, except for New York in winter and in spring and over Japan in winter where the changes occurs slightly below 8 km, and except over New York in summer and over Japan in summer and in fall where the change occurs above 10 km. A noticeable feature is that *OLT* in this region of 8–10 km altitude range get values smaller than in the planetary boundary layer. In the context of the links between the ozone trends in the UTLS region and the radiative forcing, the latter feature is important because the contribution of a perturbation on the ozone vertical profile on to the change in surface temperature is maximum in the UTLS region (Forster and Shine, 1997). Because of ceiling altitudes of MOZAIC aircraft nearly always below the tropopause over Japan in summer and fall, the positive vertical gradient of *OLT* in the lower stratosphere is not defined on the seasonal time scale. In the lower stratosphere, maximum *OLT* values are observed during spring and range from 0.9 DU/150 m over Japan to 1.4 DU/150 m in Frankfurt, minimum *OLT* values of about 0.5 DU/150 m are observed during fall. Seasonal-mean values of *MOC*, i.e. vertical integrations of thin lines, range from 34 to 50 DU and go through a maximum in spring at each MOZAIC station. With all sections of the profiles below the dynamical tropopause (Fig. 6, thick lines), seasonal climatological profiles are such that the negative vertical gradient of *OLT* extends up to the MOZAIC aircraft ceiling

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in the uppermost troposphere. Seasonal-mean values of *TOC*, i.e. vertical integrations of thick lines, range from 26 to 39 DU and go through a maximum in summer at each MOZAIC station. Very well defined maxima of *OLT* are observed in the planetary boundary layer. New York gets the highest ozone-polluted boundary layer with a maximum of 0.75 DU/150 m. An exception is for Japan where maritime-origin poor ozone air masses during the summer-monsoon season are associated with low *OLT* values up to 5 km altitude. Finally, an interesting feature of *OLT* tropospheric seasonal-mean profiles (thick lines) is their separation into two classes, i.e. spring-summer and fall-winter profiles. This classifying also shows up on the monthly basis, as seen for instance for Frankfurt (see Fig. 7). March and September appear to be transitional months between the two classes. Synthetic ozone profiles may be easily built from these averaged data for initialization purposes in chemistry-transport models and retrieval techniques for satellite products.

4.2. Seasonal cycle

The seasonal cycle of monthly-mean *TOC* over MOZAIC sites is presented on Fig. 8a. Paris and Frankfurt show a very similar seasonal cycle with a broad maximum of about 34 DU from April to August and a minimum of about 22 DU in December. The seasonal cycle over New York is similar to European cycles except for a larger range with a broad spring-summer maximum that peaks to 39 DU in June. It is interesting to note the rapid springtime increase at the three stations and then a dropping off during the late summer. The rapid springtime increase is consistent with a photochemical ozone production after ozone precursors have been accumulated in the troposphere in winter and when insolation increases. The contribution of stratosphere-troposphere exchanges to this cycle is discussed in the following section. Over Japan the seasonal cycle is quite different. The earlier springtime increase is consistent with a latitudinal effect (earlier springtime sun) as Japanese stations are the southernmost stations considered here. Winter and spring values are 2–3 DU larger than those at other sites. The cycle goes across a 38-DU maximum in June, it then abruptly falls to 28 DU during the summer-monsoon season (June–July) and slowly decreases to 25 DU in December. The four *UT* seasonal cycles (Fig. 8b) are all in phase, they display a first maximum in late spring and a second one in late summer. The amplitude is larger for New York and for Japan, in agreement with the summertime elevated tropopause there. The phasing of all four *UT* cycles suggests that the summer-monsoon over Japan does not influence the upper-tropospheric ozone budget. Mid-tropospheric contributions to *TOC* (Fig. 8c) are predominant (≈60% of *TOC*). Interestingly, the two European seasonal cycles are almost identical to the one in New York. The peak is in May-June and the minimum in December. The similarity of these three mid-tropospheric cycles has likely something to do with the homogenisation by the large-scale circulation for trace gas distributions that have a sufficient lifetime (a few weeks) like ozone. The latitudinal and the summer-monsoon effects that influence the Japanese seasonal cycle are clearly visible in the mid-troposphere. Boundary layer contributions (Fig. 8d) roughly represent a 25% contribution to *TOC*. These contributions are 10% higher in New York compare to Frankfurt and Paris during spring and summer, and are 10% higher in Japan compare to New York, Frankfurt and Paris during autumn and early spring. Local and remote anthropogenic emissions as well as biomass burning over upstream regions of Asia may be responsible of larger low- and mid-tropospheric contributions to *TOC* over Japan throughout the year except during the summer-monsoon season.

A direct comparison of our results is possible with those of Creilson et al. (2003) who use a technique based on coincident observations of the Total Ozone Mapping Spectrometer (TOMS) and stratospheric ozone profiles from the Solar Backscattered Ultraviolet (SBUV) instruments to retrieve tropospheric ozone residuals (TOR). Their Fig. 5 shows the monthly climatological tropospheric ozone residuals for two regions centered over Washington D.C. (USA) and over Bordeaux (France) together with a comparison for validation purposes with tropospheric ozone columns integrated with ozonesonde data at Wallops Island (USA) and at Hohenpeissenberg (Germany). Comparisons with our seasonal cycles for *TOC* in Frankfurt and in New York (Fig. 8a) are quite perfect with the only restriction of the underestimation in *TOC* during summertime which

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is due to a missing contribution in the upper-troposphere when tropopause-crossings by MOZAIC aircraft diminish. Summertime maximum differences can be evaluated to 1 DU in Frankfurt and 5 DU in New York.

4.3. Stratospheric Intrusion Column

The purpose here is to test the validity of the Lagrangian approach used to detect stratospheric-origin air parcels (see Sect. 3.1), and to evaluate the contribution of the stratospheric-origin ozone, i.e. the Stratospheric Intrusion Column SIC, to the Tropospheric Ozone Column TOC. Over Japan there is a large seasonal range of the frequency of flights affected by STE (i.e., $SIC>0$), from 69% in January down to 15% in August (not shown). Such a large range may be explained by favourable wintertime dynamics involving STE in the region of the subtropical jet (Sprenger et al., 2003) and by unfavourable summertime monsoon dynamics. Over Paris, Frankfurt and New York and whatever the season, about one third of the vertical profiles contains signatures of stratosphere-troposphere exchanges (not shown). The quasi-absence of seasonal variation of STE frequency over mid-latitude western stations is an indication that the criterion used here to compute SIC accumulates transient and deep events. According to Lagrangian studies exploring the sensitivity of the residence time criterion of air parcels (e.g. Wernli and Bourqui, 2002; James et al., 2003) transient and deep events lead to flat and pronounced seasonal cycles, respectively. Tropospheric depths of tropopause folds are quite variable. For instance, Danielsen et al. (1987) observed a depth that decreases from 2 to 0.6 km as the folds descends from 6 to 2 km altitude. In accordance with the latter study, the average depth of stratospheric-origin layers assessed here is 750±150 m. Monthly-mean concentrations of ozone observed in stratospheric intrusions are shown of Fig. 9a for the upper troposphere and for the mid-troposphere. Mean concentrations in the upper troposphere are always a bit higher than in the mid-troposphere for every month and every station. An upper tropospheric maximum forms in May-June, with about 150 ppbv over New York and Japan, and 110 ppbv over Paris and Frankfurt. An upper tropospheric minimum ranges from 70 to 90 ppbv during winter over the four stations. Some observed values exceed 250–300 ppbv which is indubitably of stratospheric-origin. The mid-tropospheric contribution to *SIC* falls to zero in the summer-monsoon season over Japan. With regard to ozone layer thicknesses associated with stratospheric-origin air, Fig. 9b shows the same general behaviour as for concentrations, except that this time mid-tropospheric values are always a bit larger than upper-tropospheric ones in agreement with the difference of air density. Note that springtime *OLT* affected by stratospheric intrusions are about 0.6 DU/150 m which is close to the maximum of mean *OLT* values observed in the polluted planetary boundary layer (see Fig. 6. If considering maximum isolated values, both in mid- and in upper-troposphere, it exceeds 1.0 DU/150 m which is comparable to lower-stratospheric values.

Finally, Fig. 10 shows the monthly-mean *SIC* over the four stations. The seasonal cycle exhibits a springtime maximum of about 3 DU and a minimum in autumn of about 2 DU which roughly corresponds to 10% of *TOC* throughout the year. Taking into account that several factors minimize the catching of stratospheric intrusions in our Lagrangian method (see Sect. 3.1 and 3.2), this is a strong result that confirms that the important role of stratosphere-troposphere exchanges in the tropospheric ozone budget may be further investigated with the MOZAIC dataset. Roelofs and Lelieveld (1997) considered in a numerical study that as much as 40% of tropospheric ozone may have a stratospheric origin. James et al. (2003) considered in a Lagrangian study that as much as 95% of the mass of the troposphere at any one time has been in the stratosphere within the preceding year. Our results lay the foundations of further observation-based studies where improvements for the retrieval of *SIC* from the combination of MOZAIC data and a Lagrangian approach may include i) the computation of longer backward trajectories (>5 days) to exploit the sensitivity to the residence time criterion to split transient and deep exchanges, ii) the advection with 3-hourly wind fields (analysis and 3-h forecasts slipped in between) to reduce interpolation errors due to the linear assumption on temporal changes, iii) the use of ERA40 re-analyses at ECMWF that provide better quality fields compared to operational analyses in the 1990s at the beginning of MOZAIC and allow to infer inter-annual variability in stratosphere-troposphere exchanges, iv) the comparison with a particle dispersion model (Stohl et al., 2000) where effects of turbulent mixing and deep convection are parameterized, v) the use of MOZAIC raw data (better vertical resolution with 4 s time resolution measurements, ≃20–30 m vertical resolution), vi) other MOZAIC stations to complete the mid-northern study (Washington D.C., Chicago, Vienna,. . .), vii) further verification with the MOZAIC CO measurements. However, beyond the rough assessment of SIC, we do not think that the precision of the present results allow to separately investigate inter-annual variability and short-term trends of TOC and $PTOC$. In consequence, the following section narrows on the short-term trends and inter-annual variability of TOC.

5. Short-term trends and interannual variability

The present MOZAIC 7-years dataset allows a limited investigation of the interannual variability of the tropospheric ozone column as well as an assessment of the short-term trends. First, time series of monthly-mean TOC are considered in Sect. 5.1. Then, in Sect. 5.2, the interannual variability of TOC in association with positive and negative phases of the North Atlantic Oscillation is discussed.

5.1. Short-term trends

The time series of the monthly mean TOC from August 1994 to February 2002 at the four MOZAIC sites are shown on Fig. 11. Seasonal cycles go through a minimum in winter and a maximum in summer, except for Japan where the maximum occurs during spring due to the arrival of the monsoon in summer. Stations of New York and Japan have the largest amplitude, roughly from 20 DU to 44 DU. Stations of Paris and Frankfurt have a lower amplitude, roughly from 20 DU to 36 DU, and quite similar time series (except for differences due to a better sampling over Frankfurt). Some noticeable and common features are i) high TOC values in summer 1998 over New York, Paris and

Frankfurt, ii) high *TOC* values in summer 1999 over New York and Japan, iii) highest wintertime *TOC* in 1999 over all four stations, ranging from 24 to 26 DU, iv) continuous increase of wintertime *TOC* from 1996 to 1999 at New York, Paris and Frankfurt. Visual inspection of seasonal cycles in Fig. 11 gives the impression of a positive trend. This is confirmed by a statistical linear trend analysis over the 1995–2001 period (incomplete seasonal cycles like in 1994 and in 2002 are discarded). The linear increase ranges from 0.7%/year in Frankfurt to 1.1%/year in New York.

Yearly seasonal mean *TOC* from 1994 to 2001 at the four MOZAIC sites are shown on Fig. 12. The separation in two classes, i.e. spring-summer and autumn-winter, already discussed on seasonal-mean vertical profiles (see Fig. 6), is reproduced here with the same exception of the summer-monsoon season over Japan. New York (Paris) exhibits the largest (lowest) seasonal amplitude, about 13.8 DU (9.0 DU) from the summertime mean of 37.8 DU (34.3 DU) to the wintertime mean of 24.0 DU (25.3 DU). Frankfurt and New York get the lowest wintertime mean of about 24.0 DU. Wintertime trends are positive and the strongest among the seasons, about 2%/year over New York, Paris and Frankfurt, and 1%/year over Japan. Then, in descending order, come positive trends in spring and in autumn and nearly non-existent summertime trends at the four stations. In relation to the linear increase, a wintertime bump or anomaly clearly appears in 1997 and in 1998 at all four stations. Such an anomaly is more or less well defined from autumn 1997 to summer 1999 at all stations.

Table 3 sums up the annual-mean and seasonal-mean of *TOC* (DU) and the related trends (%/year). Values are furthermore detailed for the contribution of the boundary layer, the mid-troposphere and the upper-troposphere. Wintertime noticeable features in New York, Paris and Frankfurt are the strong trends exceeding 3%/year in the boundary layer and 1.7%/year in the mid-troposphere. There are strong upper-tropospheric wintertime trends (exceeding 1.7%/year) at all stations except New York where the trend is negative (–0.7%/year). Summertime trends are generally close to zero whatever the part of the troposphere and the station, except over New York where the negative trend in the boundary layer is compensated by a positive one in

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the mid-troposphere. Finally, one can notice that whatever the station and the season, mid-tropospheric trends are always positive.

Results presented above agree well within other results found in analyses of long-term series of ozone and cited in the introduction. In particular, trends in the short-term ranging from 0.7 to 1.1%/year for *TOC* at the four MOZAIC sites are in good agreement with the longer-term positive trend of 0.7 to 1.4%/year over Central Europe reported by Weiss et al. (2001) with ozonesonde data. Further comparisons of our results with those by Naja et al. (2003) are of interest. Using residence time of air masses over Central Europe (computed from 10-days backward trajectories), Naja et al. (2003) analyse the Hohenpeissenberg and Payerne ozonesonde dataset and classify ozone observations associated with central European residence times of 4–6 days as "photochemically aged" ozone. It is shown that in the slot of 1–6 days of residence time, on average and in summer, the mixing ratio of the latter class of ozone increases at a rate of 2 ppbv per day of residence time. Then, by extrapolation to zero day of residence time (using a statistical regression model), the previous authors build a "background" ozone which is supposed to represent Atlantic air masses not influenced by European emissions. Although there is no consideration of residence time of air masses over continents in our study, three stumbling blocks with the findings by Naja et al. (2003) may be found. First, previous authors show that the "photochemically aged" ozone is maximum in summer, minimum in winter, and experiences in summertime a substantial decrease in the planetary boundary layer since the 1990s in agreement with temporal variations of Central European NO_x emissions. It is in good agreement with negative trends of *TOC* in the boundary layer found in summertime for New York and Frankfurt (see Table 3). Note that important considerations neglected in this study should be in prospect on this issue (e.g. a better definition of the top of the boundary layer, the importance of the diurnal cycle of the boundary layer, the importance of the airport position relative to its associated urban area,. . .). Second, Naja et al. (2003) show positive trends of ozone in "background' and in "photochemically aged" air in winter. It is in good agreement with the consistent positive trends found in wintertime and for the full tropospheric column at

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the four MOZAIC stations (except for New York in the upper troposphere, see Table 3). Third, Naja et al. (2003) show that "background" ozone in the planetary boundary layer and in the free troposphere has a broad maximum extending from late spring to summer, has a minimum in winter and experiences increasing influences of emissions from North America and Eastern Asia. The importance of background pollution and intercontinental transport was previously suggested by many other authors (e.g. Berntsen et al., 1996; Jacob et al., 1999; Wild and Wakimoto, 2001). The common behaviour of yearly seasonal mean TOC at the four MOZAIC stations (see Fig. 12) is strongly suggestive of a consistent influence of background pollution transported by the general circulation. Therefore, station-to-station comparisons and links with the variations of the general circulations patterns are now discussed.

5.2. General circulations patterns

The North Atlantic Oscillation (NAO) is one of the most dominant and regular patterns of atmospheric circulation variability from the United States to Siberia and from the Artic to subtropical Atlantic (Wallace and Gutzler, 1981; Barnston and Livezey, 1987). It takes the form of a dipole anomaly in the surface pressure field between Iceland and the Azores. Here we use the NAO index defined as the difference of normalized sea level pressure between Lisbon, Portugal and Reykjavik, Island (Hurrell, 1995). At the hemispheric scale, geopotential anomalies ranging from the surface to the stratosphere are dominated by a mode of variability known as the Northern Annular Mode (NAM) also called Artic Oscillation (Baldwin and Dunkerton, 1999). In order to incorporate the Japanese MOZAIC stations in our investigation we also consider NAM, which has a broader centre of action than NAO in the northern hemisphere. We use monthly-mean mid-tropospheric 1000 hpa NAM indices provided by M. Baldwin (http://www.nwra.com/resumes/baldwin/nam.php). Positive trends of NAO and AO in the last decades suggest that circulation changes may contribute to the observed winter trends of the total (stratospheric and tropospheric) ozone (Appenzeller et al., 2000; Thomson et al., 2000; Bronniman et al., 2000).

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The issue of the influence of general circulation patterns is now discussed with the aid of TOC anomalies and indices of the general circulation. With regard to relationships between NAO/NAM and TOC anomalies, two distinct effects are to be considered. Indeed, NAO/NAM variability is associated with geographical tropopause pressure patterns and with typical tropospheric transport pathways. With regard to the first effect, Appenzeller et al. (2000) have shown that the tropopause pressures are strongly correlated with a distinct geographical pattern of NAO over a large Atlantic-sector, e.g. lower tropopause over Iceland for positive NAO phases opposed to higher tropopause over Europe in positive NAO phases, and vice versa. This finding has been confirmed in a companion study (Thouret et al., 2005). With regard to the second effect, the tropospheric ozone distribution is influenced by remote sources via long-range transport, which is itself influenced by NAO/NAM inter-annual variations. Over the Atlantic the Azores high is eastward shifted of about 30° of longitude for the positive phase of NAO compared to the negative phase and the westerlies are reinforced (Cassou et al., 2004). Then, a faster and more zonal flow across the Atlantic during positive NAO phases favours the transport of anthropogenic pollution from North America to Europe (Creilson et al., 2003). As a consequence, and for the example of the Frankfurt station, NAO positive phases would be associated to positive anomalies of TOC built by a larger contribution of the upper part of the tropospheric vertical column or/and by an increase of the background tropospheric ozone.

NAO and NAM display considerable monthly and interannual variability (Hurrell, 1995), their effects reach the highest point during wintertime but have been observed at all seasons. In the construction of time series of monthly TOC anomalies (Fig. 13a), each monthly TOC is deseasonalized by subtraction of its annual-mean value (Fig. 8). To lessen the monthly variability and to capture the extra-seasonal signal shown on Fig. 12, we smooth the time series with a running window of ±6 months. The quite good overall coherence of all parameters over four major periods is striking. The period 1995–1996 shows negative TOC anomalies and negative NAO/NAM indices. It is followed by a transition year in 1997. Then comes the 1998–1999 period with positive

TOC anomalies and positive NAO/NAM indices. Finally, there is the last period 2000–2001 during which parameters show less mutual coherence and a gradual transition to negative values. Note that the most important information of Fig. 13a, i.e. the transition from a period of negative *TOC* anomalies to a period of positive anomalies, is only brought by the contribution of the mid-troposphere (not shown). Monthly time series of the contributions of the boundary layer and the upper-troposphere do not show up this transition, which suggests that the mid-tropospheric long-range transport of ozone may be a dominant process. Figure 13b shows the plot of monthly *TOC* anomalies in Frankfurt versus in New York, symbols are colour-coded with NAO indices. There exists a strong relationship between *TOC* anomalies of the two stations which is confirmed by a very high correlation factor (r=0.97, see Table 4). This correlation factor is even higher than the positive correlation factor between *TOC* anomalies at each station and NAO indices (r=0.66 for the two stations). The very high positive correlation factor between *TOC* anomalies at the two stations reinforces the latter suggestion that the long-range mid-tropospheric transport is a dominant process that establishes links between *TOC* anomalies whether the NAO phases are positive or negative. A scenario that can be proposed from our results is the following. Positive *TOC* anomalies in New York and Frankfurt during positive NAO phases are correlated by the establishment of a direct mid-tropospheric transport pathway across the Atlantic that is favoured by a zonalisation of the flow during positive NAO phases. During negative NAO phases, this direct transport pathway is somewhat disrupted by meridional perturbations of the mid-tropospheric flow as shown by Creilson et al. (2003) and the correlation between *TOC* anomalies could be lessened by this effect. However, climatological conditions prevailing during negative NAO phases may lead to independent negative *TOC* anomalies on both sides of the Atlantic, which finally would reinforce indirectly the correlation between *TOC* anomalies, i.e. without the establishment of a direct link with regard to the transport. From Figs. 13c and d and Table 4, it can be seen that the extension of the previous scenario to the hemispheric scale by introducing the Japanese station is unlikely because of the lessening of the correlation between *TOC* anomalies and NAM

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indices. Now, considering the positive anomaly that has been defined from autumn 1997 to summer 1999 at all stations (Fig. 12) in the present 7-years dataset, such anomaly has a strong contribution to the common behaviour of TOC related parameters, i.e. multi-stations positive short-term trends, multi-stations positive correlations with NAO/NAM variations, and inter-stations correlated anomalies. The winter of 1997–1998, marked by a record breaking El Nino event, was the second warmest winter since 1895. Global temperatures in 1998 were the warmest in the past 119 years and the previous record was set in 1997 (see the Annual Review on climate of 1998 on the NOOA web site at http://lwf.ncdc.noaa.gov/oa/climate/research/1998/ann/ann98.html). These warmer conditions may have globally favoured the photochemical production of ozone in the troposphere, what coupled to the transition towards positive NAO/NAM indices, may have also favoured the long-range transport of higher background concentrations of ozone. Whether or not the transition of negative to positive NAO phases in this period could be a response to anthropogenic forcings, as suggested by some scenario model experiments in which enhanced greenhouse gas concentrations are prescribed (Ulbrich and Christoph, 1999), or may be better understood in terms of an intrinsic dynamical property of the North Atlantic atmosphere (Cassou et al., 2004) is out of the scope of the present study.

6. Conclusions

We have investigated climatological and interannual variability aspects of ozone vertical profiles performed at four stations, Frankfurt (Germany), Paris (France), New York (USA) and the cluster of Tokyo, Nagoya and Osaka (Japan), by commercial aircraft participating to the MOZAIC program from August 1994 to February 2002. This database of several thousands of vertical profiles constitutes nowadays one of the most interesting datasets with regard to research issues on the tropospheric ozone budget and recent short-term trends. The study focuses on the analysis of two vertical integrated quantities in the troposphere, i.e. the Tropospheric Ozone Column (TOC), which is the vertical integration of ozone from the ground to the dynamical tropopause, and the Stratospheric Intrusion Column (*SIC*), which is the vertical integration of stratospheric-origin ozone throughout the troposphere. Commercial aircraft generally fly in the range 9–12 km altitude, so that ascent and descent profiles at airport do not systematically include the tropopause region. Taking into account the interest of working on a maximum of vertical profiles and the necessity to have profiles in the full depth of the troposphere (to compute the integrated quantities), our strategy has been to fill up unexplored parts of the vertical profiles as much as possible with seasonal climatological profiles. This avoids to bias the results towards meteorological situations for which the tropopause is systematically low. The impact that the filling-up process may have on the investigation of short-term trends by introducing a constant in the dataset is limited to the summertime uppermost troposphere in New York and Japan.

The climatological analysis shows that the *TOC* seasonal cycle ranges from a minimum wintertime of about 22–25 DU at all four stations to a spring-summer maximum of about 35 DU in Frankfurt and Paris, and 38 DU in New York. Over Japan, the maximum occurs in spring because of the earlier springtime sun, then the invasion of monsoon air masses in the boundary layer and in the mid-troposphere steeply diminishes the summertime *TOC*. Boundary layer contributions to *TOC* are 10% higher in New York compare to Frankfurt and Paris during spring and summer, and are 10% higher in Japan compare to New York, Frankfurt and Paris during autumn and early spring. Local and remote anthropogenic emissions as well as biomass burning over upstream regions of Asia may be responsible of larger low- and mid-tropospheric contributions to *TOC* over Japan throughout the year except during the summer-monsoon season.

A simple Lagrangian analysis based on 24-h backward trajectories of air masses has shown that the contribution of *SIC* to *TOC* exhibits a springtime maximum of about 3 DU and a minimum in autumn of about 2 DU, which roughly corresponds to 10% of stratospheric-origin ozone into the troposphere throughout the year. As this simple analysis minimizes the stratospheric source, it confirms the important role of stratosphere-troposphere exchanges in the tropospheric ozone budget and prompts to improve the Lagrangian approach proposed here to more deeply investigate the issue with the MOZAIC dataset.

The investigation on the short-term trends of the tropospheric ozone column over the period 1995–2001 has shown a linear increase of 0.7%/year in Frankfurt, 0.8%/year in Japan, 0.9%/year in Paris, and 1.1%/year in New York. This is in agreement with longer-term positive trend of 0.7 to 1.4%/year over Central Europe reported by Weiss et al. (2001) with ozonesonde data. Results show that essential ingredients to the positive short-term trends are the continuous increase of wintertime TOC from 1996 to 1999 and the contributions of the mid-troposphere whatever the season. Slightly negative short-term trends of the contributions of the boundary layer to TOC in New York and Frankfurt may be an indication of decreasing NO_x emissions. Summertime ozone does not seem to contribute to the positive short-term trends, though relatively higher summertime TOC have been recorded in 1998 for New York, Paris and Frankfurt and in 1999 for New York and Japan. Some considerations involving possible effects of large-scale circulations patterns variability like the North Atlantic Oscillation and the Northern Annular mode have been discussed. The transition from a period of negative TOC anomalies before 1997 to a period of positive TOC anomalies in 1998–1999 comes with a shift from negative to positive phases of the North Atlantic Oscillation that seems to be a determining factor in the positive short-term trends observed in New York, Frankfurt and Paris.

Appendix: Computation of the Tropospheric Ozone Column (TOC)

For a volume of gas V measured at pressure P and temperature T, it is possible to define its volume V_s altered to standard pressure P_s=101 325 Pa and standard temperature T_s=273, 15 K, referring to the Ideal Gas Law:

$$\frac{P \cdot V}{T} = \frac{P_s \cdot V_s}{T_s}$$

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which can be also written as:

$$\rho = \rho_s \cdot \frac{T_s}{T} \cdot \frac{P}{P_s} \tag{1}$$

where ρ and ρ_s are the density and the standard density of air.

Then, using Eq. (1), if we apply the definition of partial pressure, we find the ozone number density (molecules per unit volume, $\rho_{(O_3)}$) with:

$$\rho_{(O_3)} = \frac{N_A}{V} \cdot \frac{T_s}{T} \cdot \frac{P_{p(O_3)}}{P_s} \tag{2}$$

where, N_A is Avogadro's number (N_A=6,022·10^{23}) and V the volume of air (V=22,4 l). The ratio N_A/V is the number of molecules per unit volume of air, i.e. Loschmit number (ρ_s).

In Eq. (2), T is the temperature at the pressure P of MOZAIC ozone measurement and $P_{p(O_3)}$ the corresponding partial pressure deduced from the ozone mixing ratio $r_{m(O_3)}$ given in ppbv, with following relation:

$$P_{p(O_3)} = r_{m(O_3)} \cdot P \tag{3}$$

Replacing constant values in Eq. (2), we find, in mol·cm^{-3}:

$$\rho_{(O_3)} = 7,2425 \cdot 10^{16} \cdot \frac{P_{p(O_3)}}{T} \tag{4}$$

The ozone thickness of the MOZAIC basic layer (h=150 m), expressed in DU, will be called Ozone Layer Thickness (*OLT*). We will used *OLT* to evaluate MOZAIC Ozone Column (*MOC*) in DU, which is integration of *OLT* over MOZAIC vertical column (Fig. 2).

To obtain *OLT* in DU, we introduce in Eq. (4), the depth of the basic layer (h=150 m) and the conversion factor from mol·cm^{-2} to DU:

$$OLT = \frac{7,2425 \cdot 10^{16}}{2,6861 \cdot 10^{16}} \cdot \frac{P_{p(O_3)}}{T} \cdot h \cdot 10^2 \tag{5}$$

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and combining Eqs. (3) and (5) we find OLT:

$$OLT = 4,044 \cdot 10^{-5} \cdot \frac{r_{m(O_3)} \cdot P}{T} \quad (6)$$

In Eq. (6), P is in Pa, $r_{m(O_3)}$ in ppbv, T in K and OLT in DU/150 m.

Tropospheric Ozone Column (TOC, expressed in DU) is the integration of OLT from ground up to the dynamical tropopause (DT):

$$TOC = \sum_{ground}^{DT} OLT \quad (7)$$

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Table 1. List of used abbreviations.

Abbreviation	Signification	Comment
RH	Relative Humidity	in %
PV	Potential Vorticity	in pvu
RPV	Reconstructed Potential Vorticity	in pvu
DT	Dynamical Tropopause	–
DU	Dobson Unit	–
OLT	Ozone Layer Thickness	in DU/150 m
MOC	MOZAIC Ozone Column	in DU
TOC	Tropospheric Ozone Column	in DU
TOR	Tropospheric Ozone Residuals	in DU (Creilson et al., 2003)
dTOC	Deseasonalized TOC	in DU
PTOC	Pure Tropospheric Ozone Column	in DU
SIC	Stratospheric Intrusion Column	in DU
BL	Boundary Layer	from ground to 2 km
MT	Mid Troposphere	from 2 km to 8 km
UT	Upper Troposphere	from 8 km to DT
UTLS	Upper Troposphere Low Stratosphere	–
STE	Stratosphere Troposphere Exchange	–
NAO	North Atlantic Oscillation	–
NAM	Northern Annular Mode	–

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Table 2. Statistics on MOZAIC vertical profiles available between August 1994 and February 2002 at the four stations: **P** is the number of total available vertical profiles; **P1** is the number of vertical profiles for which aircraft have crossed the dynamical tropopause; **P2** is the number of vertical profiles that have been filled up to the dynamical tropopause with the corresponding part of the seasonal-average tropospheric *OLT* profile (see Fig. 6); **P3** is the number of vertical profiles unavailable for the study because PV data are missing; **P4** is the number of vertical profiles for which the aircraft did not cross the tropopause and for which the tropopause of the day is above the highest altitude level defined by the seasonal-average tropospheric *OLT* profile. Values in brackets are corresponding percentages.

Station	P	P1	P2	P3	P4
FRANKFURT	6338	2813 (44.4)	3015 (47.6)	100 (1.6)	410 (6.5)
PARIS	3308	1307 (39.5)	1662 (50.2)	45 (1.4)	294 (8.9)
New York	2631	881 (33.5)	1006 (38.2)	25 (1.0)	719 (27.3)
JAPAN	1899	360 (19.0)	481 (25.3)	23 (1.2)	1035 (54.5)

Table 3. Annual- and seasonal-mean of *TOC* (DU), and corresponding short-term trends (%/year) for the entire troposphere and for boundary layer (*BL*, 0–2 km altitude), mid-troposphere (*MT*, 2–8 km altitude) and upper-troposphere (*UT*, 8 km altitude to the dynamical tropopause *DT*) over New York, Paris, Frankfurt and Japan.

		ANNUAL		SPRING		SUMMER		FALL		WINTER	
		DU	%/year	DU	%/year	DU	%/year	DU	%/year	DU	%/year
	TOC	*30.3*	*1.1*	*33.4*	*1.5*	*37.8*	*0.0*	*26.8*	*0.8*	*24.0*	*1.9*
New York 2631 profiles	TOC in BL	7.2	0.4	8.3	1.2	9.4	−1.2	6.2	1.2	5.4	3.9
	TOC in MT	17.9	1.2	20.0	1.2	20.3	0.6	16.2	1.0	15.6	2.0
	TOC in UT	5.5	1.3	5.7	1.6	8.1	0.1	4.8	−0.1	3.8	−0.7
	TOC	*29.5*	*0.9*	*32.5*	*0.5*	*34.3*	*0.2*	*26.2*	*0.4*	*25.3*	*2.0*
PARIS 3308 profiles	TOC in BL	6.8	0.9	7.9	0.3	7.8	0.3	5.8	0.6	5.8	3.1
	TOC in MT	17.7	1.5	19.5	1.4	20.0	0.4	16.0	0.7	15.5	1.8
	TOC in UT	5.2	−0.1	5.5	−0.9	6.6	−0.4	4.6	−0.2	4.2	1.9
	TOC	*28.5*	*0.7*	*32.0*	*1.3*	*34.0*	*0.0*	*25.1*	*0.3*	*23.9*	*2.0*
FRANKFURT 6338 profiles	TOC in BL	6.2	0.3	7.5	0.5	7.7	−0.2	5.1	0.7	5.0	3.3
	TOC in MT	17.7	0.7	19.6	1.5	20.3	0.0	16.0	0.3	15.3	1.7
	TOC in UT	4.9	0.8	5.3	1.2	6.2	0.2	4.2	0.0	4.0	1.7
	TOC	*30.2*	*0.8*	*36.1*	*0.9*	*31.5*	*0.1*	*27.5*	*0.8*	*26.4*	*1.0*
JAPAN 1899 profiles	TOC in BL	7.4	−0.1	9.5	0.5	6.4	0.1	6.6	0.3	7.1	0.3
	TOC in MT	17.8	0.8	21.3	1.0	17.8	0.1	16.1	1.0	16.4	1.0
	TOC in UT	5.4	1.0	5.9	−0.4	7.2	0.3	5.0	1.1	3.5	3.7

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Table 4. Parameters deduced from linear regression fit between TOC anomalies (noted TOC') themselves and between TOC anomalies and NAO or NAM indices over Frankfurt, New York and Japan (see Fig. 13). a and b are parameters of the linear regression fit, r is the correlation factor and σ the standard deviation.

TOC'/TOC'	**a**	**b**	**r**	σ
Frankfurt–New York	1.51	0.08	0.97	0.31
Frankfurt–Japan	1.17	0.11	0.89	0.47
New York–Japan	0.73	0.07	0.89	0.48
TOC'/NAO	**a**	**b**	**r**	σ
Frankfurt	0.41	−0.26	0.66	0.38
New York	0.26	−0.28	0.66	0.38
TOC'/NAM	**a**	**b**	**r**	σ
Japan	0.05	−0.16	0.33	0.16

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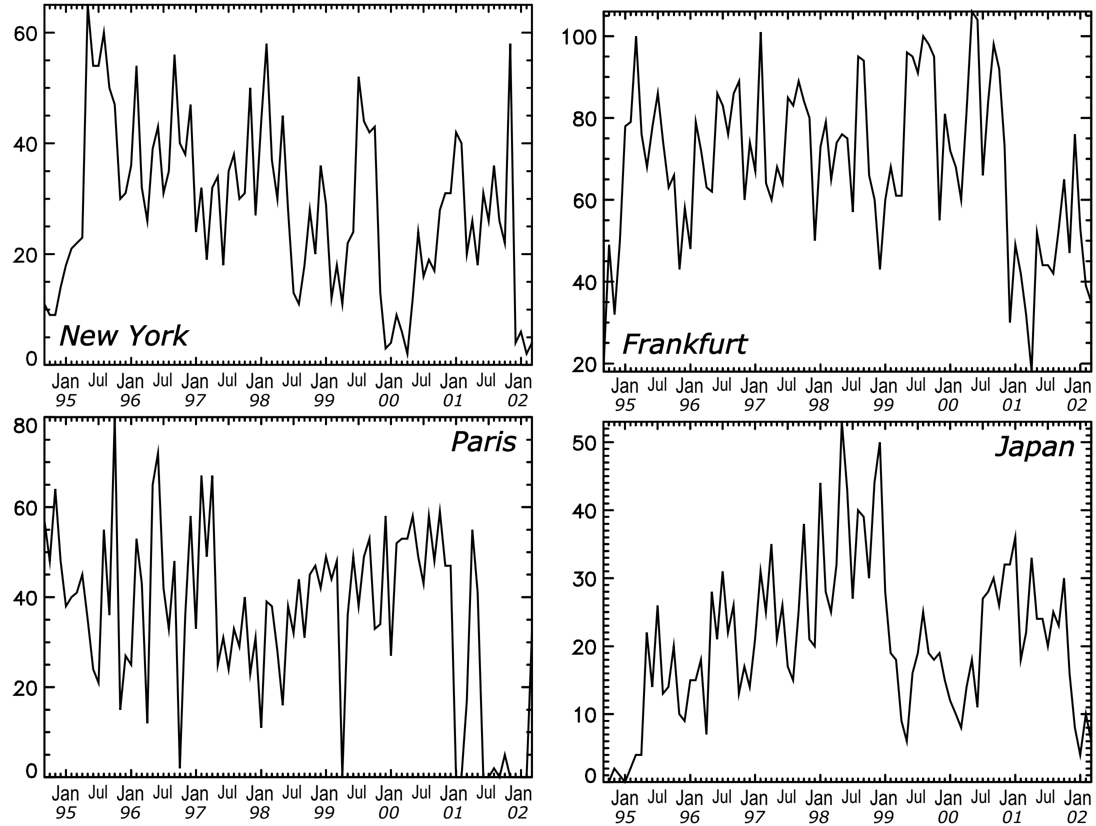

Fig. 1. Number of MOZAIC per month profiles over the 1994–2002 period for New York, Paris, Frankfurt and Japan stations.

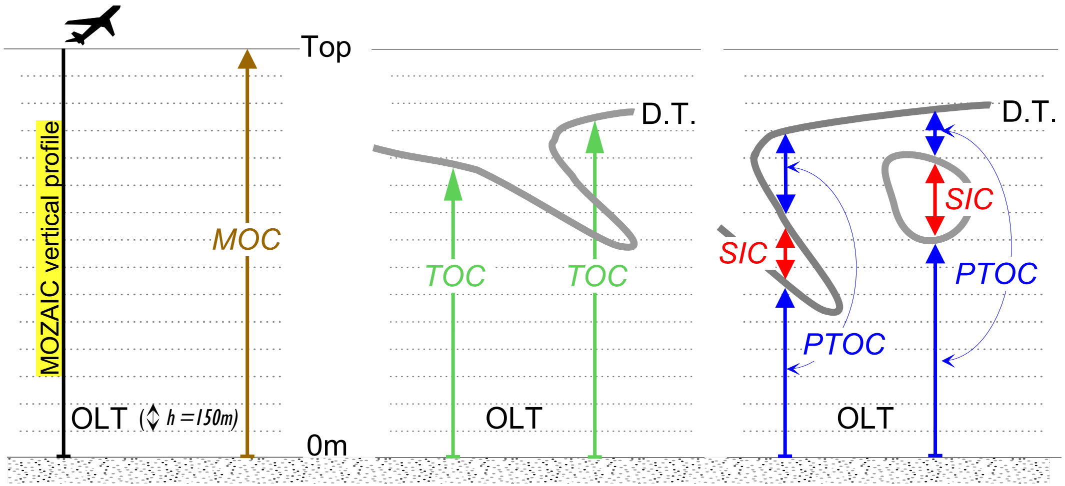

Fig. 2. Schematic definitions: Ozone Layer Thickness (*OLT*) is the equivalent amount of ozone expressed in DU (see Appendix) for a 150-m deep layer where full-resolution MOZAIC ozone data are averaged. MOZAIC Ozone Column (*MOC*) is the integrated ozone profile from the ground to the cruise altitude of the aircraft (noted Top). Tropospheric Ozone Column (*TOC*) is the integrated ozone profile from the ground to the Dynamical Tropopause (*DT*, see text for details). Stratospheric Intrusion Column (*SIC*) is the integrated ozone profile through layers that fulfil stratospheric-origin criteria below the dynamical tropopause (see text for details). Pure Tropospheric Ozone Column (*PTOC*) is the difference between *TOC* and *SIC*.

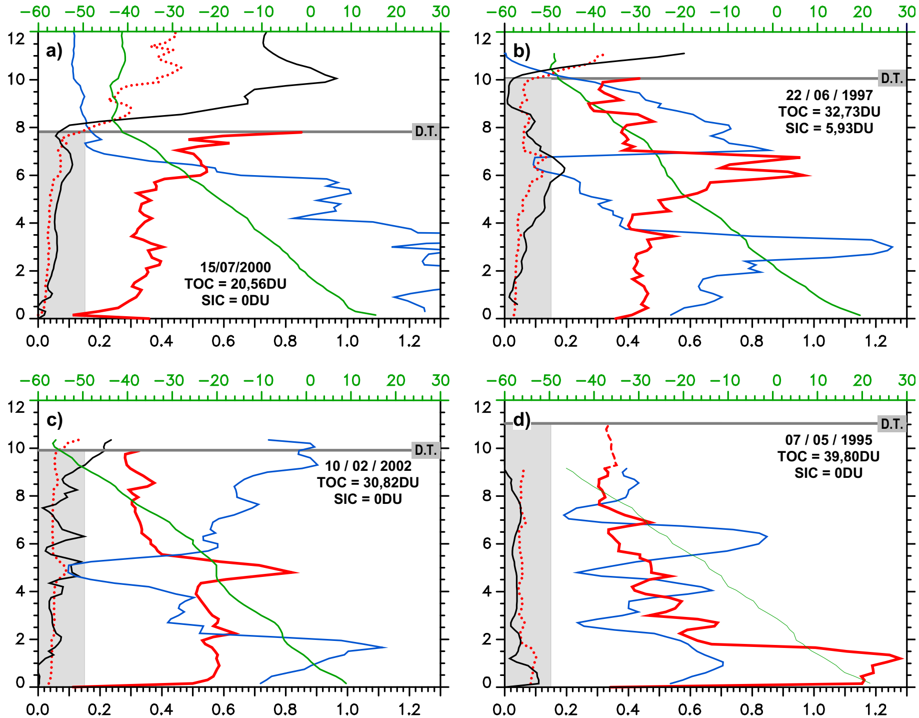

Fig. 3. Individual MOZAIC vertical profiles (in km) over Frankfurt. Horizontal bottom scale is available for ozone mixing ratio [in ppmv – red dotted line], *OLT* [in DU – red solid line or red dashed line if the profile has been filled up to the altitude of the dynamical tropopause using the monthly-average *OLT* profile], relative humidity [×100% – blue line] and reconstructed potential vorticity [×10 pvu – black line]. Horizontal top green scale is temperature [°C – green line]. *TOC* is computed over a column from the ground to the *DT* [dark grey horizontal line]. A tropospheric layer contributes to *SIC* if three criteria are met: altitude between 2 km and the *DT*, relative humidity lower than 50% and reconstructed potential vorticity exceeding 1.5 pvu (i.e. if the black line exits on the right of the shade grey pattern).

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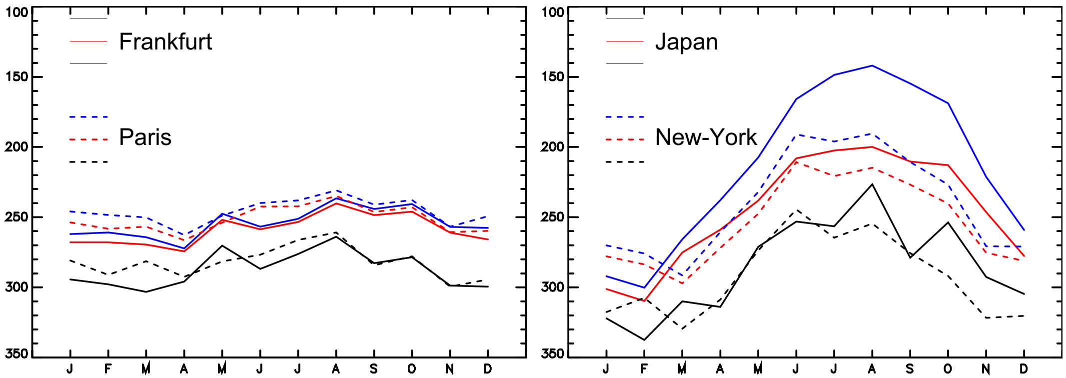

Fig. 4. Monthly-mean pressures of the dynamical tropopause *DT* (in hPa) deduced with a *PV* threshold (2 pvu) on ECMWF analyses at the four stations: blue lines stand for *DT* sampled at the frequency of MOZAIC aircraft, black lines stand for *DT* sampled at the frequency of MOZAIC profiles that cross the tropopause (column P1 in Table 2), and red lines stand for *DT* with the sampling frequency of MOZAIC profiles that cross the tropopause or that have been filled up to it (columns P1, P2 and P4 in Table 2, see text for details).

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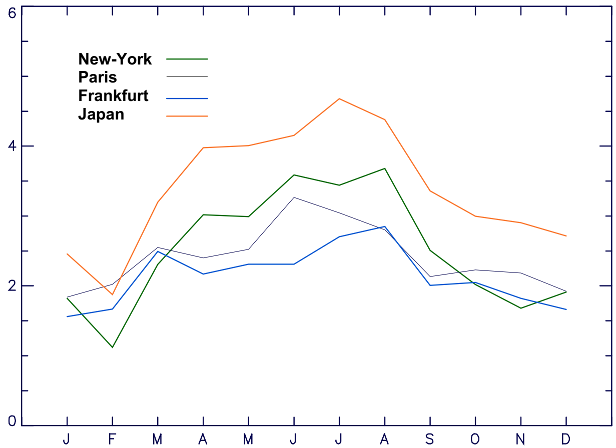

Fig. 5. Monthly-mean contribution to the Tropospheric Ozone Column (DU) by the filling-up process applied on MOZAIC vertical profiles in columns P2 and P4 of Table 2.

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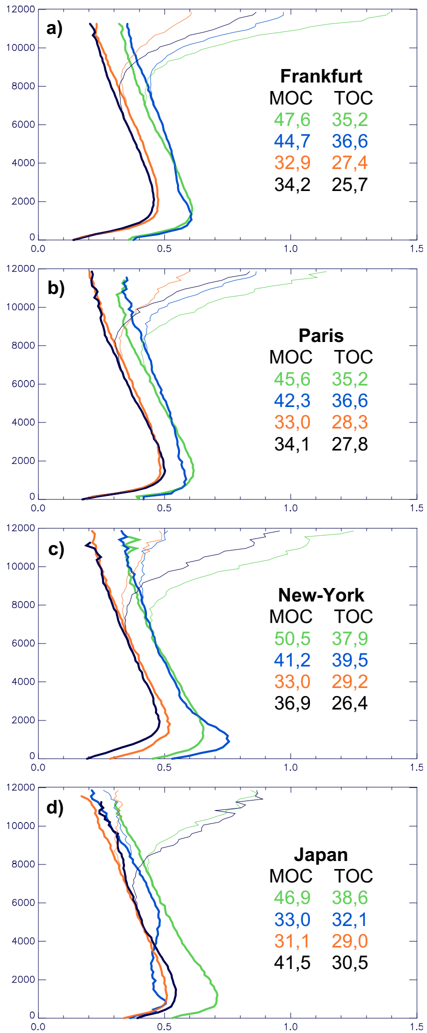

Fig. 6. Seasonal climatological vertical profiles (in m) of Ozone Layer Thickness (*OLT*, in DU/150 m). (Thin lines): no distinction is made with regard to the altitude of the dynamical tropopause. Vertical integrals are the seasonal climatological *MOC* (DU). (Thick lines): made with sections of the profiles below the dynamical tropopause. Vertical integrals are the seasonal climatological *TOC* (DU). Colors: green for spring, blue for summer, orange for fall and black for winter.

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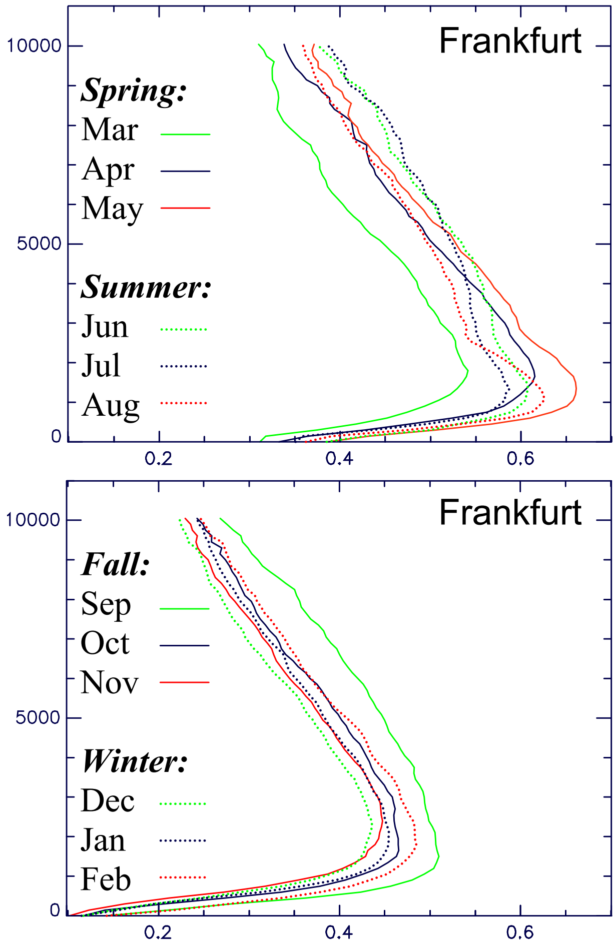

Fig. 7. Monthly-mean tropospheric profiles (in m) of *OLT* (DU/150 m) over Frankfurt.

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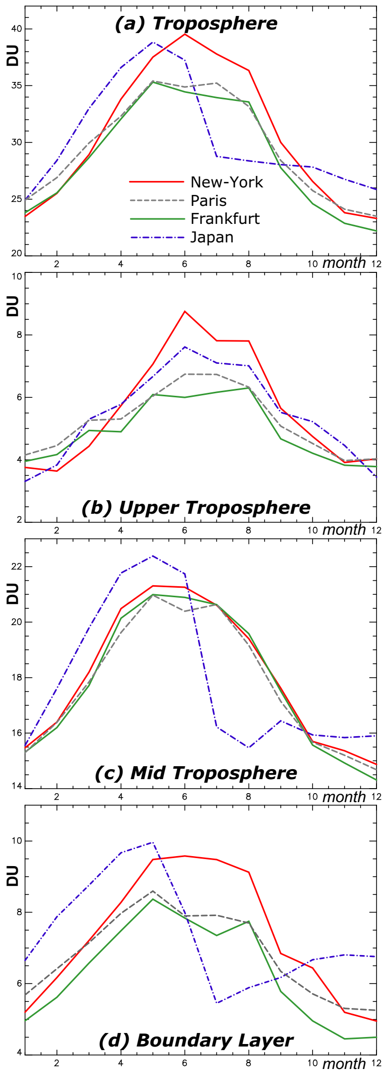

Fig. 8. Monthly-mean *TOC* seasonal cycle: **(a)** Total tropospheric contribution, **(b)** Upper-Tropospheric contribution, **(c)** Mid-Tropospheric contribution, **(d)** Boundary Layer contribution. New York (red line), Paris (dashed black line), Frankfurt (green line) and Japan (dashed-dot blue line).

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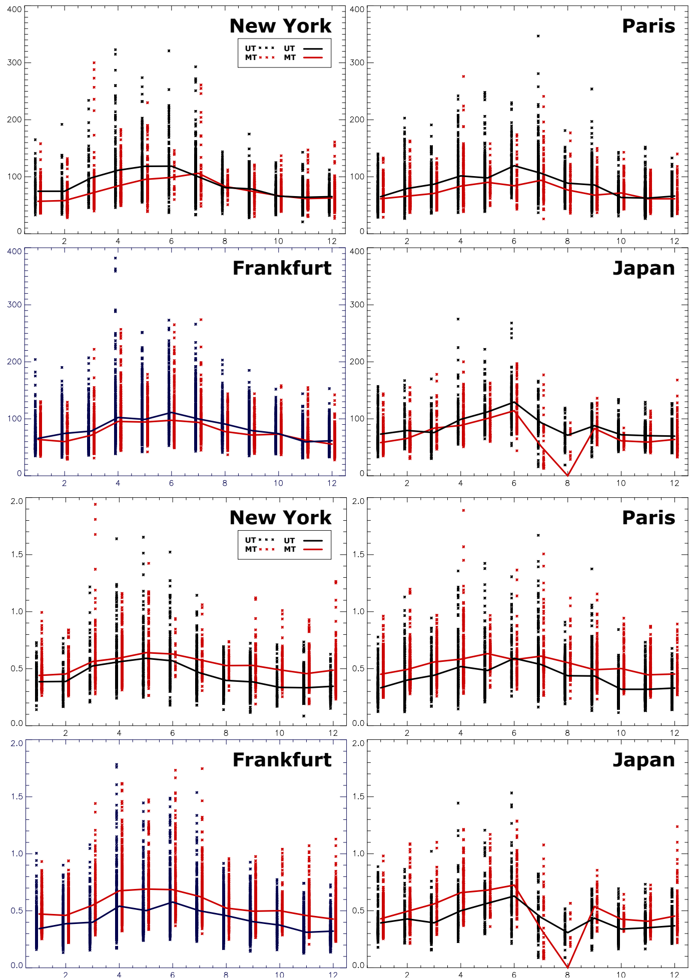

Fig. 9. (Top) Monthly-mean ozone concentration (ppbv) of 150 m-deep layers affected by stratosphere troposphere exchanges for the mid-troposphere (red line) and for the upper-troposphere (black line) over the four MOZAIC stations. (Bottom) Same as the top panel but for the ozone layer thickness (DU/150 m). In both panels the red (black) points correspond to individual observations in the mid-troposphere (upper troposphere).

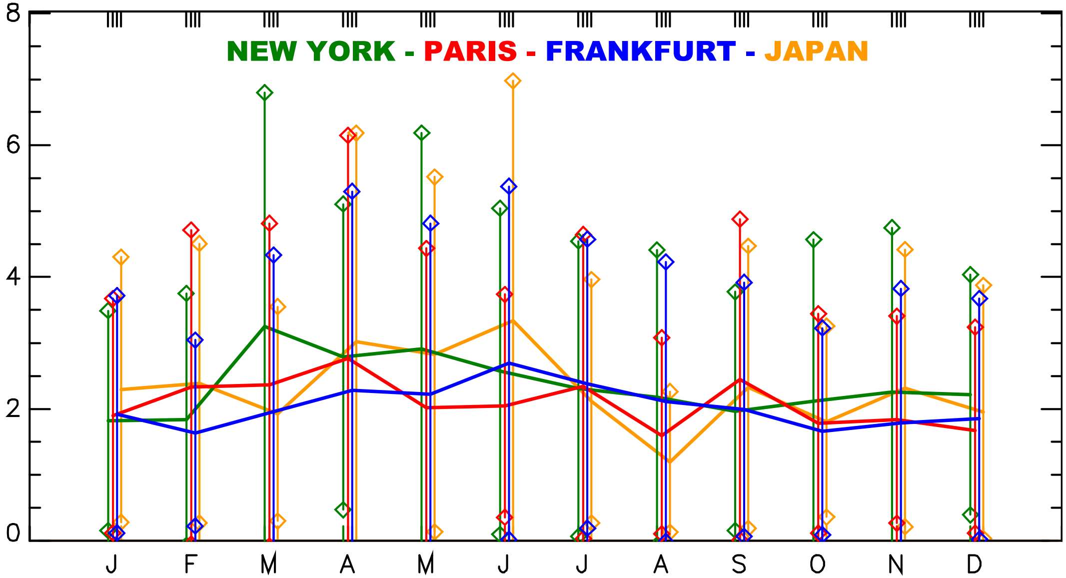

Fig. 10. Monthly-mean values of the Stratospheric Intrusion Column (*SIC* in DU), i.e. the integrated ozone profile through tropospheric layers that fulfil stratospheric-origin criteria. Vertical bars represent the standard deviations (DU). Color code: blue for Frankfurt, red for Paris, green for New York, and orange for Japan

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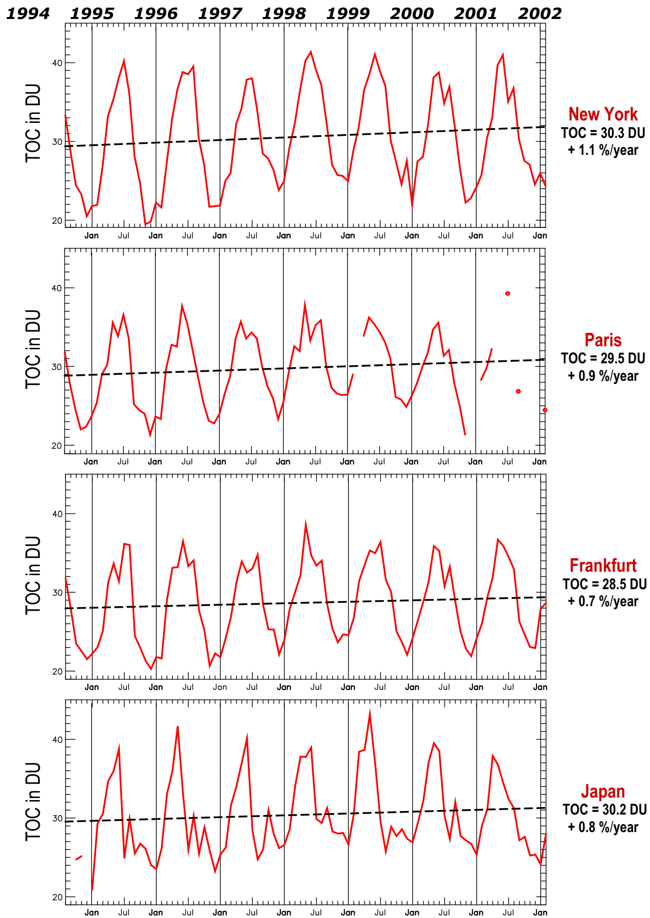

Fig. 11. Time series of monthly mean Tropospheric Ozone Column *TOC* (DU, red solid lines) from August 1994 to February 2002 for the 4 MOZAIC stations. Indication on the right summarize the annual-mean *TOC* (DU) and short-term trends (%/year) for the 1995–2001 period.

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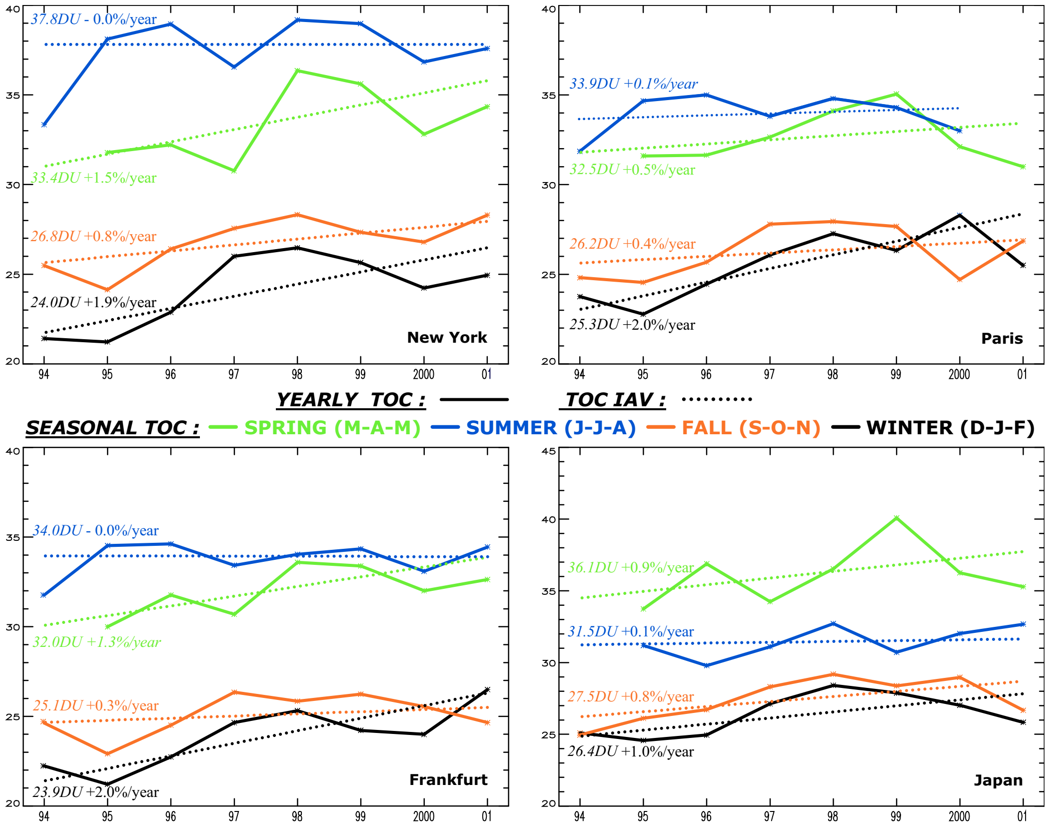

Fig. 12. Yearly seasonal-means for Tropospheric Ozone Column (DU) from 1994 to 2001 for the 4 MOZAIC stations (solid lines, green for spring, blue for summer, orange for autumn, black for winter). Dotted lines are the linear regression fits. Averaged seasonal-mean *TOC* (DU) and seasonal linear increase (%/year) computed for the 1995–2001 period are displayed on the left part of each plot.

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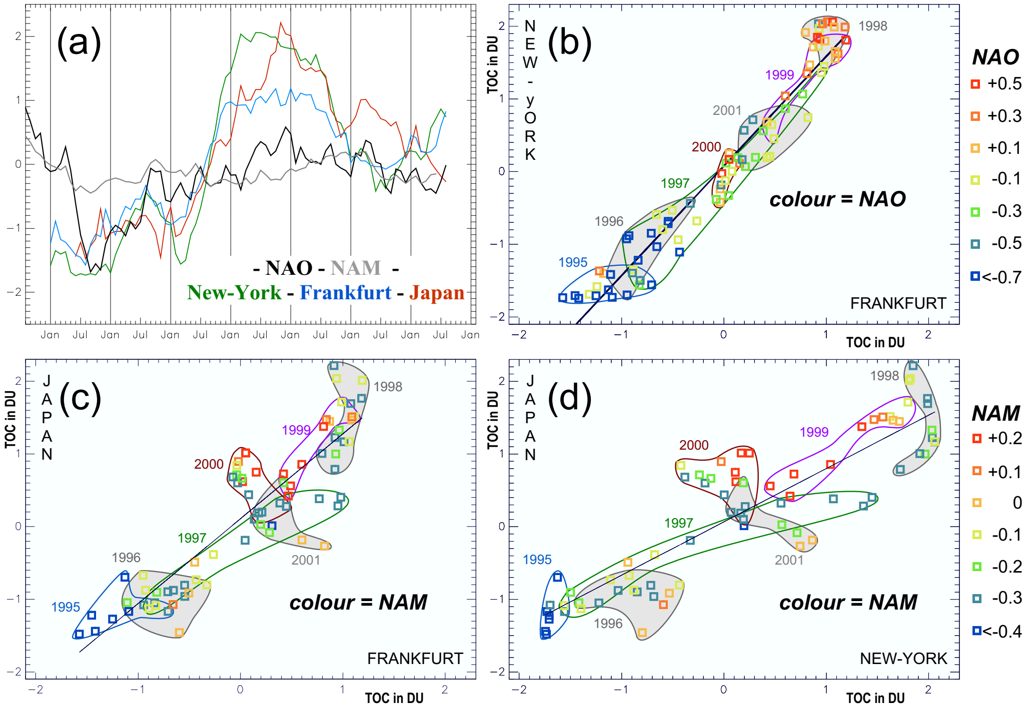

Fig. 13. (a): Time series from 1995 to 2001 of monthly *TOC* anomalies (DU) in New York (green line), Frankfurt (blue line) and Japan (red line) and of indices for NAO (black lines) and NAM (grey line). **(b)**: Monthly *TOC* anomalies (DU) in New York versus monthly *TOC* anomalies (DU) in Frankfurt. Months are symbolized by a square. A coloured line encircles months of one year. The colour of each square is coded with the NAO index scaled regularly in 7 classes between −0.7 to 0.5 as given on the right part of the figure. The black line indicates the linear regression that best fits inter-station *TOC* anomalies (see Table 4). **(c)**: as for (b) but for Japan versus Frankfurt and for the NAM index at 500 hPa. The colour of each square is coded with the NAM index scaled regularly in 7 classes between −0.4 to 0.2 as given on the right part of the figure. **(d)**: as for (c) but for Japan versus New York.

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