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TELLUS

Cross-tropopause fluxes of ozone using assimilation of MOZAIC observations in a global CTM

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ABSTRACT

Ozone measurements from Measurements of OZone and wAter vapour by aIrbus in-service airCraft (MOZAIC) have been assimilated into the global chemical transport model of Météo France known as Modèle de Chimie Atmosphérique à Grande Echelle (MOCAGE). The assimilation makes improvements to the free model simulations of ozone in the upper troposphere and lower stratosphere, which are generally overestimated in the tropical region and underestimated in mid-latitudes. The tropical–subtropical gradient of ozone is also improved following assimilation and comparison with vertical profiles from ozonesondes suggests that the assimilation leads to a better representation of the vertical gradient around the tropopause. We use the assimilated fields to calculate a value for the flux of ozone across the tropopause. The net flux of ozone from stratosphere to troposphere is found to be 451 Tg yr^{-1} before assimilation and 383 Tg yr^{-1} after assimilation. The downward flux of ozone in the mid-latitudes exhibits an annual cycle with maximum flux occurring in early spring and minimum flux in autumn.

1. Introduction

Determining the amount of cross-tropopause transport of chemical species is important for understanding the chemistry and climate of the upper troposphere and lower stratosphere (UTLS). Ozone is of great importance to climate due to its radiative effects (Ramanathan et al., 1987), and as an oxidant it plays a role in the chemistry of the region. Estimates of global net fluxes calculated from models span a range of values from 1400 Tg yr^{-1} (Crutzen et al., 1999) to 340 Tg yr^{-1} (Horowitz et al., 2003) indicating some deficiencies in the modelling and understanding of the region. Observational based studies, such as Gettelman et al. (1997) who used data from the Upper Atmosphere Research Satellite or Murphy and Fahey (1994) using correlations of N_2O with O_3 observed by research aircraft, gave a range of values for the net ozone flux of between 590 and 450 Tg yr^{-1}. Models are now beginning to approach these values as a recent study by Stevenson et al. (2006) suggests. The 25 models in Stevenson et al. (2006) gave values for the ozone flux as 550 ± 150 Tg yr^{-1}.

The range of values reflects not only the method used, but also the the surface taken to represent the tropopause across which the fluxes are calculated. In the tropics, the tropopause coincides roughly with an isentropic surface of 380 K and in the extratropics with a surface of constant potential vorticity of about 2 potential vorticity units (PVU) (1 PVU = 10^6 K kg^{-1} m^2 s^{-1} Holton et al. 1995). The region above 380 K which is reached from the troposphere by diabatic motion was termed by Holton et al. (1995) as the 'overworld'. In the extratropics, where isentropes cross the tropopause, the term 'lowermost stratosphere' was coined. The tropical tropopause can be better represented as a layer, extending from about 355 to 450 K (e.g. Sherwood and Dessler, 2000), on ascending through which, the air gradually loses its tropospheric characteristics and becomes more stratospheric in nature. Similarly, the relationships between stratospheric and tropospheric chemical tracers (Fischer et al., 2000; Hoor et al., 2002; Pan et al., 2004) suggest that the extratropical tropopause can also be described as a layer, spanning a broad range of potential vorticity (PV) values. For the purpose of flux calculations however, the concept of a simple dividing-line is extremely useful, and surfaces between 1.6 and 3.5 PVU have been used (WMO, 1986; Hoerling et al., 1991) in studies.

In this paper, we calculate the flux of ozone across the tropopause using a 3-D global chemical transport model known as Modèle de Chimie Atmosphérique à Grande Echelle (MOCAGE, Peuch et al., 1999) which was developed at Météo France. One reason for calculating the cross-tropopause flux from a chemical transport model, is that the model offers consistent 3-D dynamical fields and global ozone fields. However, the disadvantage might be a lack of confidence in the simulated

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ozone fields. We address this concern by assimilating reliable observations of ozone from the Measurements of OZone and wAter vapour by aIrbus in-service airCraft (MOZAIC) project (Marenco et al., 1998) following the method depicted in Cathala et al. (2003). Data assimilation allows us to combine information from the model and from observations in an optimal way considering the errors in both sources.

The method of assimilation developed by Cathala et al. (2003), is specifically adapted for the in situ measurements from MOZAIC which have a good resolution in the northern hemisphere but limited coverage in the southern hemisphere and over the Pacific. Computing global fluxes from MOZAIC data alone is not feasible. The assimilation is based on 'ozone equivalent latitude' and allows the data to have an impact on the model over a wider area and over several days. The method modifies gradients in the concentrations of ozone whilst preserving the structure and form of the ozone fields. The MOZAIC data are available along flight levels in the UTLS, an area which is of great scientific interest but which is not well represented by atmospheric chemistry models (Law et al., 2000). Data assimilation is particularly useful for improving the gradients of ozone in the crucial region around the tropopause and hence to improve the estimates of the flux of ozone across the tropopause.

The following section describes the model, the data and the assimilation method. We then compare the raw and assimilated ozone fields in Section 3 and then calculate the flux across the tropopause in Section 4.

2. Data and method

The MOZAIC project uses sensors which are mounted on five commercial aircraft to obtain in situ measurements of various chemical species in the atmosphere. The majority of measurements are made at cruise altitude, between 9 and 12 km or 285 and 195 hPa. The coverage for the northern hemisphere is good with the highest density of measurements along the north Atlantic flight corridor, but the Pacific and the southern hemisphere are rarely sampled. Details of the MOZAIC project can be found in Marenco et al. (1998).

The MOCAGE 3-D chemistry and transport model (Peuch et al., 1999) was developed at Météo France and became operational in 2003 for chemical weather forecasts (Dufour et al., 2005; http://www.prevair.org/fr/index.php). The chemical scheme, RACMOBUS, employed by the model for this study, is a combination of the stratospheric scheme REPROBUS (Lefèvre et al., 1994) and the tropospheric scheme RACM (Stockwell et al., 1997). RACMOBUS includes 119 individual species or groups of species along with 372 chemical reactions and also includes dry deposition (Michou and Peuch, 2002; Nho-Kim et al., 2004; Michou et al., 2005) and scavenging (Mari et al., 2000). Emissions are prescribed following the International Global Atmospheric Chemistry/Global Emission Inventory Activity (IGAC/GEIA) and Emission Database for Global Atmospheric Research (EDGAR) inventories given at 1° resolution and based on annual averages (Michou and Peuch, 2002).

The model has a semi-Lagrangian advection scheme (Williamson and Rasch, 1989) using cubic polynomial interpolation in all three directions. The semi-Lagrangian advection scheme has been tested within REPROBUS in multiyear simulations (WMO, 1998). The model can use up to four nested domains, but only one domain is used here, having a horizontal resolution of $2^\circ \times 2^\circ$. The vertical grid is composed of 47 hybrid (σ, P) levels from the surface to 5 hPa with a resolution of about 800 m in the region of the UTLS. The convection scheme is that of Bechtold et al. (2001). The performance of the model regarding transport at resolved and subgrid scales are described and evaluated by Josse et al. (2004). MOCAGE is an off-line model and is driven by Météo France's six-hourly operational analyses known as ARPEGE (Courtier et al., 1991) with the vertical velocity being calculated from the horizontal wind components.

Chemical data assimilation is increasingly employed in MOCAGE as a way of constraining the distributions of observed species (and also possibly of non-observed but chemically related species) while meteorological analyses give realistic forcing. Pradier et al. (2006) have assimilated CO data from the Measurements of Pollution in the Troposphere (MOPITT) (Drummond and Mand, 1996) instrument. The assimilation provided global 4-D fields which are well suited for budget analyses. MOCAGE is also part of the first international exercise of ozone assimilation (Geer et al., 2006).

Cathala et al. (2003) described the assimilation of ozone data from the raw MOZAIC measurements into the MOCAGE model and we summarize the main points of the assimilation method here. The method of assimilation was developed as a way of ensuring that the limited temporal and spatial coverage of MOZAIC data had a global impact. Data assimilation is an effective way of improving the gradient of ozone in the UTLS as the strong gradient of ozone around the tropopause is difficult for models to capture. The assimilation gave best results when performed in a 'non-local' or 'flow-following' coordinate system based on ozone equivalent latitude as the horizontal coordinate and potential temperature as the vertical (O3EL, θ). Analogous to PV equivalent latitude, the ozone equivalent latitude corresponding to a given ozone isovalue on a given isentrope is defined as the value of the geographical latitude that encompasses a surface area of the same size. An advantage of this method is that a single observation can have an impact over the whole surface corresponding to the same values of O3EL and potential temperature. MOZAIC measurements with potential temperatures greater than 310 K are assimilated.

The observations from MOZAIC during a 24 h period, centred at 12UTC, are transformed into assimilation space (O3EL, θ). The observations in this one day time-slot provide a set of 'super-observations' for each (O3EL, θ) gridcell in assimilation space. Super-observations that fall with a radius of influence around each gridpoint provide a weighted contribution to the

value at the gridpoint, the weights being decreasing functions of the distance in O3EL and θ between the observation and the gridpoint (Cathala et al., 2003). The super-observations are thus the average of the observations that fall within a cell in assimilation space. Given that MOCAGE is an off-line model, there is no feedback between the model and the meteorological forcings. Thus, the assimilation of the ozone measurements affects only the model's ozone fields with no feedback on dynamics and radiation. The wind and temperature fields are therefore the same in both the assimilated and non-assimilated cases and any difference to the ozone flux is not due to a change in the height of the dynamical tropopause.

To evaluate the success of the assimilation, we use independent measurements of ozone from the World Ozone and Ultraviolet Radiation Data Centre's (WOUDC) ozonesondes. These ozonesondes were launched from over 300 sites around the world but for our purposes we concentrate on the sites which are closest to the MOZAIC network and which have at least 5 d per month from which to make a monthly-mean profile. They are supplemented by the Southern Hemisphere Additional Ozonesondes (SHADOZ; Thompson et al., 2003), which are launched from a series of stations in the southern hemisphere tropics. The frequency of these measurements is on average one per week at each station so we have at best four vertical profiles available for each site every month. The advantage of using SHADOZ sondes is that the sites are situated in areas which are not well covered by MOZAIC, and therefore the effect of the assimilation of MOZAIC data can be determined at sites far from its implementation and the non-local effects of the assimilation can be measured.

3. Ozone fields

The aim of this paper is to calculate the flux of ozone across the tropopause combining the advantages of the global ozone fields and 3-D dynamical fields available from the MOCAGE model. One disadvantage of this approach might be a lack of confidence in the simulated ozone fields and we address this concern by assimilating reliable ozone observations from MOZAIC into the model. Thus in this section, we demonstrate the effects of the assimilation on the raw ozone fields from the model through comparisons with both dependent and independent data.

Seasonal climatologies of ozone from MOZAIC, based on the years 1994–1996, were described in detail in Thouret et al. (1998). Following the method of Thouret et al., we create seasonal averages from both the daily MOZAIC data and the daily assimilated ozone data at 200 hPa. The method, in which the mean value for each flight crossing the cell is calculated before averaging these mean values to give an average value for the cell, is used to account for the problems arising from the different path lengths of flights within each cell. The cells in this instance are $5^\circ \times 5^\circ$. To obtain output from the model on the aircraft trajectories, an on-line interpolation is performed from the model's grid to the aircraft trajectory every hour. The seasonal climatologies are then constructed in the same way as for the observations.

We begin by illustrating the effect of the assimilation on the dependent data set, that is, MOZAIC to show that the assimilation does indeed approach the observations. Figures 1 and 2 show the climatology of ozone from the measurements and for the modelled fields before and after assimilation for two seasons in 2000, March–April–May (MAM) and September–October–November (SON), respectively.

The seasonal differences evident in these plots are discussed in Thouret et al. (1998). The differences reflect both the seasonal variability in the position of the tropopause leading to a greater or lesser percentage of stratospheric measurements compared with tropospheric measurements, and true seasonal variability due to production, transport or photochemistry of ozone. In the tropics, where the flights are in the upper troposphere in both seasons, there is little seasonal variation with ozone concentrations of less than 80 ppbv being common. The low values can be explained by the photochemical depletion of ozone in the presence of high humidity (Thouret et al., 1998) and the transport by convection of ozone-poor air from the boundary layer. The model tends to overestimate the observed concentrations by about 40 ppbv in the tropical region in both seasons.

Outside the tropical region, seasonal differences are complicated by the seasonal movements in the position of the tropopause relative to the cruise altitudes of the aircraft as this determines whether the air sampled is stratospheric or tropospheric. Using 100 ppbv of ozone as a rough indication of the position of the tropopause, we can see that the boundary of tropospheric air lies near 30°N in MAM and slightly further north in SON. The meridional gradient of ozone is not very well captured by the model. In SON (Fig. 2), the range of mixing ratios is reduced compared with the observations and the assimilation can be seen to make a big improvement.

The ozone concentrations at higher latitudes, north of about 60°N, where the air sampled by MOZAIC is primarily stratospheric, are greater in MAM compared with SON which is likely to be due to the descent of ozone-rich air from higher in the stratosphere. In this region, the model tends to underestimate the ozone concentrations. Over the north atlantic flight corridor, the MOCAGE model underestimates the amount of ozone by up to 80 ppbv. The biggest improvements following the assimilation are seen in this region, as the MOZAIC flights are the most frequent there.

The effects of the assimilation scheme on the absolute values of ozone from the model is summarized in Fig. 3 for the whole of the year 2000. The top panel shows the number of ozone observations in each 20 ppbv bin. The distribution peaks at 40–60 ppbv and tails off slowly with values of ozone greater than 280 ppbv being quite common. Whilst the range of values from the model is similar to the observations, the distribution is displaced towards the higher end of the scale (100–120 ppbv) as MOCAGE generally overestimates the observed values of

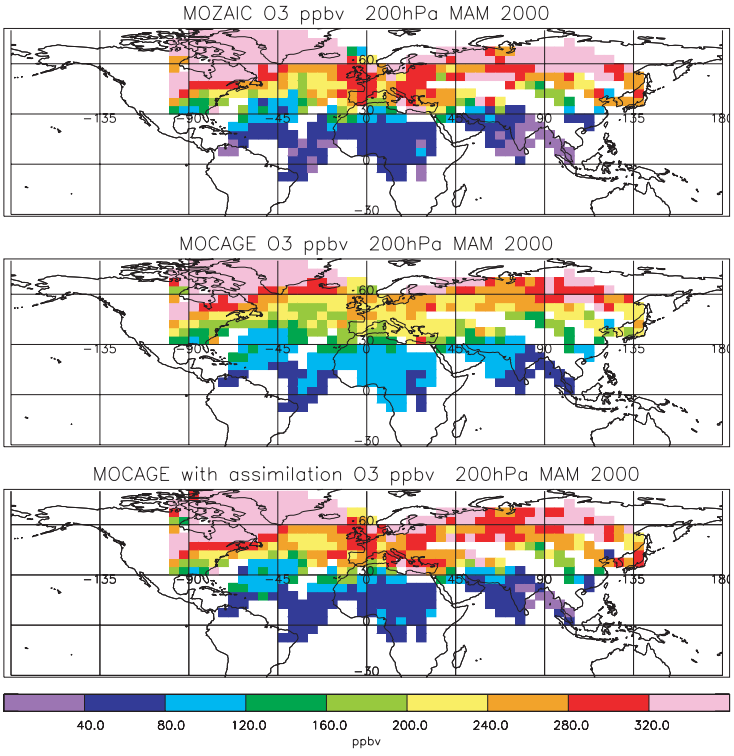

Fig. 1. Global ozone values from MOZAIC observations and the MOCAGE model without assimilation, and with assimilation for MAM 2000.

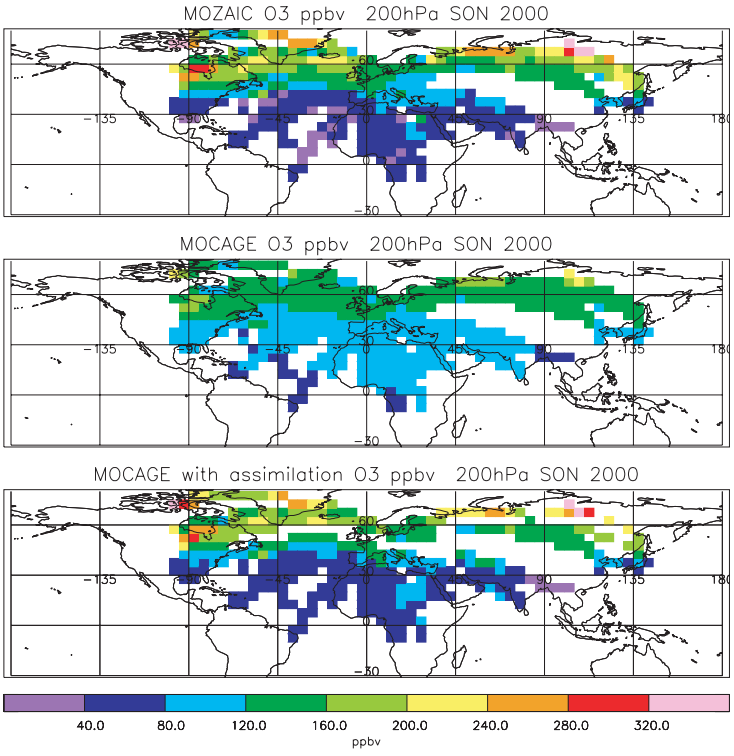

Fig. 2. Global ozone values from MOZAIC observations and the MOCAGE model without assimilation, and with assimilation for SON 2000.

ozone. The concentrations tail-off much more quickly and there are fewer observations greater than 280 ppbv than were apparent in the observations. The effect of the assimilation is seen in the third panel to have shifted the distribution back towards that of the observations with the peak being found at 60–80 ppbv. The tail of the distribution has been flattened relative to the model with no assimilation and resembles more closely that of the dependent observations.

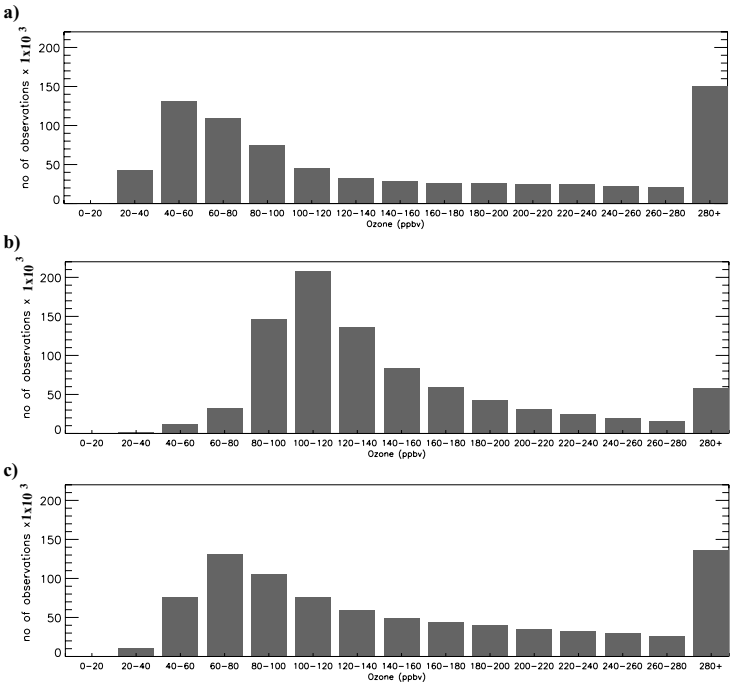

Fig. 3. Global ozone values at 200 hPa for the year 2000 from (a) the MOZAIC observations, (b) the model without assimilation and (c) the model with assimilation.

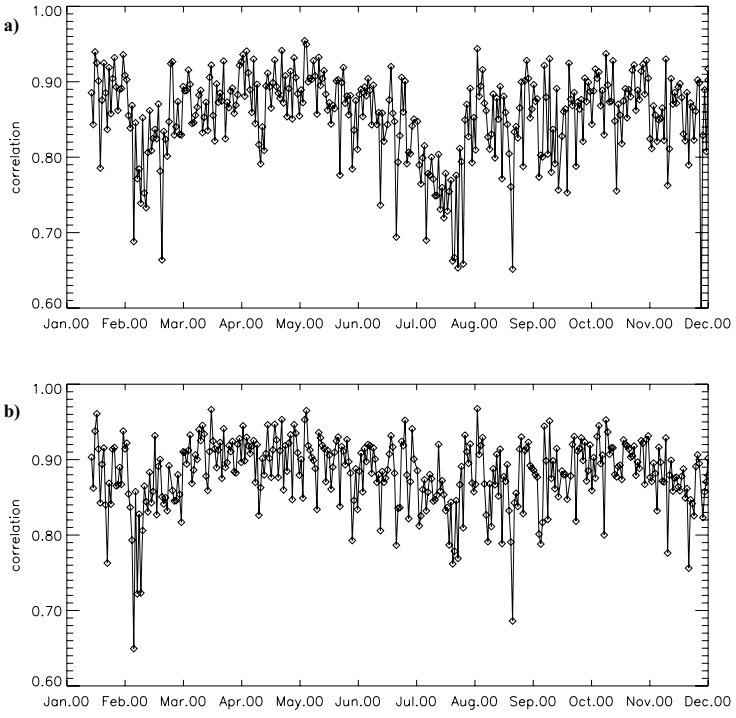

Fig. 4. Daily correlation between MOZAIC and MOCAGE at 200 hPa (a) before and (b) after the assimilation of MOZAIC ozone data.

Figure 4 shows a time-series of the daily correlation between the MOZAIC and MOCAGE ozone data in the 5° cells for the year 2000. In the top panel, the correlation is between MOZAIC and MOCAGE before assimilation. The correlation is generally about 0.84 but during JJA it drops to around 0.79, due to a poorer representation of the chemistry and transport during times when convection is strong. The bottom panel shows the correlation between MOZAIC and MOCAGE after assimilation. There is no significant improvement to the annually averaged correlation (0.87 after assimilation cf. 0.84 before assimilation) but the assimilation greatly improves the poor correlation in JJA from 0.79 to 0.86. We have shown that the assimilation is effective in relaxing the model back towards the observations. We show that this has improved the gradient of ozone around the tropopause and

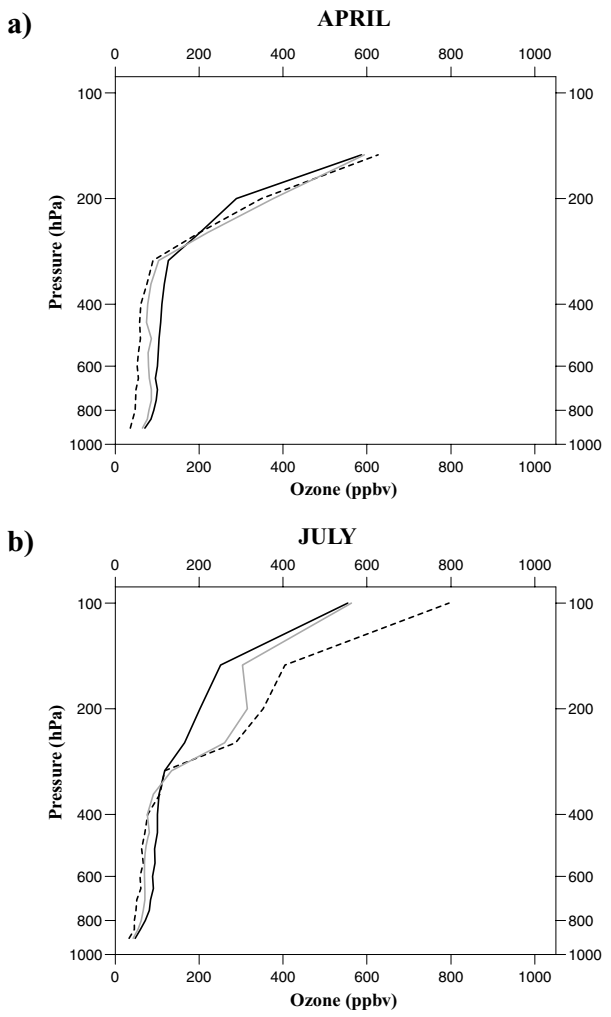

Fig. 5. Vertical profiles of monthly averaged ozone for (a) April and (b) July from WOUDC ozonesonde at Hohenpeissenberg (48 °N, 11°E). The dashed line indicates the radiosonde observations, the solid black line indicates the model run without assimilation of MOZAIC data and the grey line shows the model run with assimilation of MOZAIC data.

has an effect on the model at locations remote from the MOZAIC network.

We now focus on comparing the assimilated data with independent data and for this we use profiles of ozone from ozonesondes which were part of the WOUDC and SHADOZ programmes. Figure 5 shows the monthly averaged vertical profile of ozone from the WOUDC station at Hohenpeissenberg (48°N, 11°E) in Germany during April and July. There were on average 10 soundings per month throughout January to September 2000 making it one of the more favourable stations for comparison with the model. The underestimation of ozone in the stratosphere and overestimation in the upper troposphere (as seen in Figs 1 and 2) leads to a smearing out of the gradient of ozone around the tropopause. This behaviour was also seen when profiles of ozone from the TOMCAT model were compared with MOZAIC data (Law et al., 1998). Data between 310 and 380 K are assimilated but the main effects of the assimilation are felt in the region 300–190 hPa, corresponding to the range of cruise altitudes of the aircraft. In this region, assimilation is seen to increase the concentration of ozone in the lower stratosphere and decrease its concentration in the upper troposphere, thus improving the gradient of ozone around the tropopause. There is little impact on levels above about 150 hPa as this is well above the maximum cruise-altitude of 196 hPa for the aircraft. In the lower troposphere in the extratropics, improvements are seen in the assimilated fields due to the impact of assimilating the data near 310 K which occasionally captures part of the quasi-vertical profiles during the landing and take-off of the MOZAIC aircraft.

The difficulties in capturing the tropical to subtropical gradient of ozone and the gradient of ozone near the tropopause has been seen in other models (Law et al., 2000). Law et al. (2000) suggested that this might be due to an insufficient vertical resolution near the tropopause. In model intercomparison studies, Roelofs et al. (2003) and Meloen et al. (2003) noted that models with low vertical resolution and semi-Lagrangian advection schemes tended to be more diffusive and smear-out the gradients of ozone in regions where the gradients are strong. Both of these factors are likely to be important in MOCAGE as it too uses a semi-Lagrangian advection scheme and although the vertical resolution is better than those of the models in the Law et al. study it remains insufficient to represent the strong gradients near the tropopause.

At locations further from the MOZAIC network, we assessed the impact of the assimilation on vertical profiles of ozone as compared with the SHADOZ ozonesondes. In general, the impact of the assimilation is to offer some improvement to the modelled profiles. Figure 6 illustrates the monthly averaged profiles of ozone for Ascension and Reunion. For Reunion in May (6 a), the ozone concentrations were overestimated by the model at all altitudes. The poorer performance of the model in the tropical region represents problems associated with transport and scavenging. At Reunion Island in particular, the ozone profiles are less well simulated by the model than at other ozonesonde stations (Cathala, 2004). They are frequently affected by stratospheric intrusions and by the transport of ozone and its precursors from Africa and Madagascar (Randriambelo et al., 2000). The emissions used in the present simulation are based on an annual mean and may be unrepresentative of this period given that it is well before the onset of biomass burning. As we will see in the following section, stratosphere to troposphere transport is overestimated in the southern hemisphere which may have contributed to the overestimation of ozone compared with the ozonesonde profile for Reunion island. The assimilation has led to an overall improvement in the modelled profile with a general decrease in the ozone concentration over the whole profile.

In part (b) of Fig 6 the assimilated profile for Ascension lies further from the observed profiles in the mid-troposphere

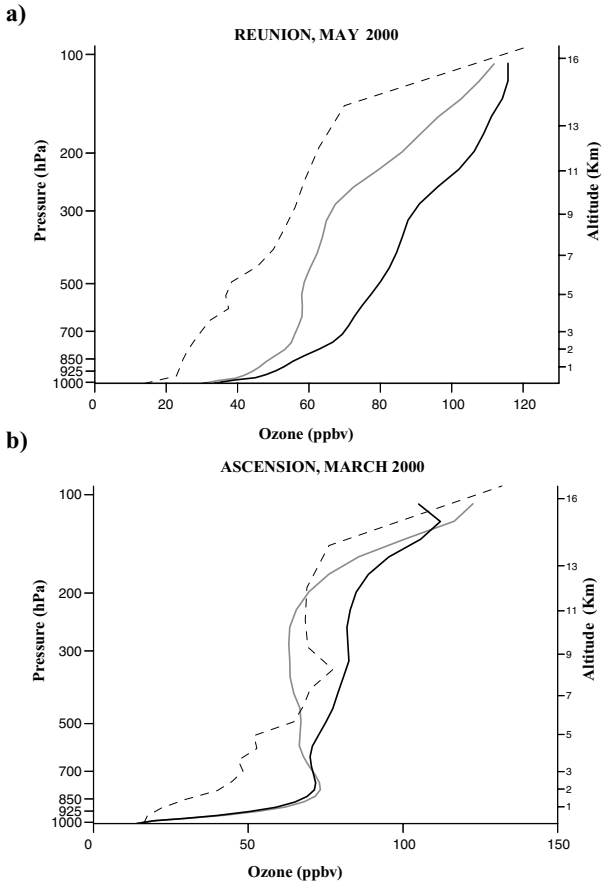

Fig. 6. Vertical profiles of monthly averaged ozone from SHADOZ ozonesondes at (a) Reunion in May (21°S, 55°E) and (b) Ascension in March (8°S, 14°W). The dashed line indicates the radiosonde observations, the solid black line indicates the model run without assimilation of MOZAIC data and the grey line shows the model run with assimilation of MOZAIC ozone data.

at around 400 hPa but more closely approaches the observed profile in the upper troposphere. The fact that the assimilation of MOZAIC data, which is primarily in the northern hemisphere can work to improve vertical profiles at locations far from the MOZAIC measurement tracks illustrates the advantages of the non-local assimilation technique. Further improvements could be be achieved through assimilation of data which has coverage in the southern hemisphere. Recent experiments with Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) data suggest that profiles of ozone from satellites may give sufficient information in the upper troposphere to be useful for assimilation (Geer et al., 2006).

4. Ozone fluxes

In the previous section, the assimilation scheme was introduced. Through evaluation against dependent and independent data, we showed that the analyses for the year 2000 were improved by the assimilation as compared with the previous estimates from the model. We use these ozone fields to calculate the flux of ozone across the tropopause. There are many ways to estimate the flux of ozone across the tropopause, for example, by correlation of concentrations of N_2O with O_3 (Murphy and Fahey, 1994) or by correlation of column ozone and column PV (Olsen et al., 2002, 2003), contour advection (Jing et al., 2004), or chemical transport modelling (e.g. Crutzen et al., 1999).

Here, we apply the formula of Wei (1987) and as described in Grewe and Dameris (1996), to calculate fluxes from the MOCAGE fields before and after the assimilation of MOZAIC ozone data. The advantage of this method is that we have all the required dynamical information from the model, along with the global estimates of ozone, improved through the assimilation of the MOZAIC observations. The formula can be expressed with geometric height as the vertical coordinate as:

$$F_z(\mathrm{O_3}) = \rho \,.\, \mathrm{O_3}\left(\omega - \frac{\delta z_{\mathrm{trop}}}{\delta t} - \overrightarrow{V_h} \,.\, \overrightarrow{\nabla}_{\mathrm{trop}} z_{\mathrm{trop}}\right) \quad (1)$$

with ρ as the density of air, O_3 the mixing ratio of ozone, ω the vertical velocity, $\overrightarrow{V_h}$ horizontal wind, and z_{trop} the height of the tropopause. For more details of the derivation of this equation see Wirth and Egger (1999). Wirth and Egger (1999) used five different methods to determine the exchange of mass for a synoptic-scale case-study. Three of these methods were based on different formulations of eq. (1), using pressure, potential temperature or potential vorticity as vertical coordinates. They found that some versions of the Wei equation performed better than others. There was sometimes a cancelation of terms, and inconsistencies with the diagnosed location and orientation of the tropopause. Wei's formula with potential vorticity as vertical coordinate performed better than those expressions with pressure or potential temperature as vertical coordinates. However, when only net fluxes are considered, the calculation of cross tropopause fluxes should be independent of the choice of vertical coordinate (Wei, 1995) and thus in this article we calculate only the net fluxes. The net flux is defined as the difference between the stratosphere to troposphere (STT) that is, downward flux and the troposphere to stratosphere (TST), that is, upward flux (Stohl et al., 2003).

For the calculation of the cross tropopause fluxes using equation 1 we must determine the height of the tropopause. Grewe and Dameris (1996) summarized the sensitivity of the flux calculation to the definition and position of the tropopause. In most studies, the dynamical tropopause is used, based on potential vorticity and expressed in PVU ($1\,\mathrm{PVU} = \times\, 10^6\,\mathrm{K\,kg^{-1}\,m^2\,s^{-1}}$). The mid-latitude tropopause is generally found between 1.6 PVU (WMO 1986) and 3.5 PVU (Hoerling et al., 1991) and we have chosen to use a value of 2 PVU which lies within this range. For the tropical tropopause, where the PV surface is ill-conditioned, we use the 380 K isentrope (Holton et al., 1995). After determining the height of the tropopause at each gridpoint, the flux

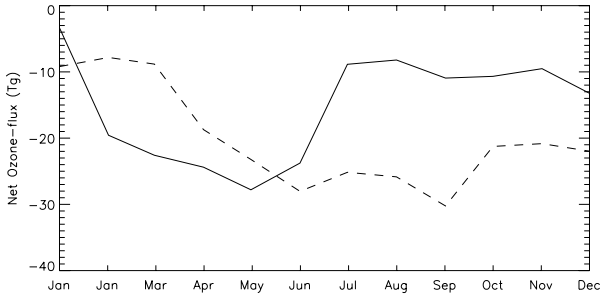

Fig. 7. Monthly averaged net flux of ozone across the ±2 PVU surface for the northern hemisphere extratropics (solid line) and southern hemisphere extratropics (dashed line), calculated from the model after the assimilation of MOZAIC ozone.

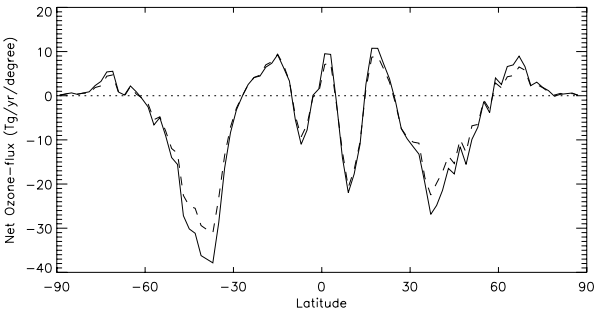

Fig. 8. Annual net flux of ozone across the ±2 PVU surface (or 380 K surface in the tropics) per latitude band calculated from MOCAGE before assimilation (solid line) and after the assimilation (dashed line) of MOZAIC ozone. Net flux towards the troposphere is marked as negative.

of ozone across the surface is calculated. The flux calculations are performed on the 6-hourly fields from the model.

Figure 7 shows the monthly averaged net flux of ozone for the mid-latitudes (30–60°) northern and southern hemispheres. The net flux, being the difference between the STT and TST fluxes, is towards the troposphere as the downward component is greater than the upward component; this has been given a negative sign. The results are consistent with the annual variation of net ozone fluxes shown by Olsen et al. (2004). In the northern hemisphere an annual cycle is evident with the largest negative value of the net flux being in MAM with smaller values in SON. The southern hemisphere annual cycle is out-of-phase with that in the northern hemisphere with the maximum net flux seen in September.

We find that the southern hemisphere has a higher net ozone flux than the northern hemisphere. For the case without assimilation 42% is in the NH compared with 58% for the SH. After assimilation 45% is in the NH compared with 55% for the SH. In comparison, Roelofs and Lelieveld (1995) reported 59% of the net flux in the northern hemisphere and we would expect a stronger contribution from the northern hemisphere due to greater stratospheric wave-driving. The results after assimilation have improved the hemispheric differences slightly, towards the expected greater flux into the northern hemisphere. As there is an underestimation of ozone concentration in the lower stratosphere of both hemispheres, the effects of this are more evident in the northern hemisphere where the transport component of the flux is greater. After the assimilation, which increases the ozone concentrations and which has more effect in the northern hemisphere, there is a corresponding increase in the contribution to the fluxes from the northern hemisphere at the expense of the contribution from the southern hemisphere.

The variation in the net flux with latitude is shown in Fig. 8 calculated from the model with and without assimilation. The maximum flux occurs in the extratropical region near 30° in both hemispheres and remains strong throughout the mid-latitudes. The graph takes a similar form to zonally averaged net mass fluxes, (Gettelman and Sobel, 2000) and net ozone fluxes Grewe (2006) but we find bigger upward and downward ozone fluxes in the tropical region due to the Wei equation being less well defined there. Over the tropical region however, these upward and downward fluxes cancel out so that the biggest contribution to the total global net flux occurs outside the tropics.

The net global flux across the tropopause calculated by MOCAGE is 451 Tg yr^{-1} without assimilation and 383 Tg yr^{-1} with assimilation. The value for the net flux after assimilation is smaller than that before assimilation even though the values of ozone in the lower stratosphere generally increased following the assimilation. This is explained in Fig. 9 which shows, for each season, the difference in the zonal means of ozone between the non-assimilated and assimilated runs. The assimilation has biggest impact in the northern hemisphere which is what we would expect given the distribution of the MOZAIC measurements. The main increases in ozone are not found in regions directly adjacent to the 2 PVU tropopause. Between 20 and 40°N, the tropopause is found in a region which has experienced very little change in ozone. Poleward of 40°N the 2 PVU tropopause tends to lie in a region where the ozone concentration has actually diminished which may account for the reduction in the ST ozone flux following the assimilation.

Our estimations with and without assimilation fall at the lower end of estimations which range from about 1400 Tg yr^{-1} (Crutzen et al., 1999) to 340 Tg yr^{-1} (Horowitz et al., 2003). However, there has been a tendency for estimates to be revised downwards in the light of results from a number of observational based studies. For example, Gettelman et al. (1997) used data from the Upper Atmosphere Research Satellite and estimated the value for the ozone-flux across the 100 hPa surface as between 450 and 590 Tg yr^{-1}, and Murphy and Fahey (1994) estimated 450 Tg yr^{-1} from correlations of concentrations of N_2O with O_3 observed by research aircraft. Models are now approaching these values and our estimates fall within the range 520 ± 200 Tg yr^{-1} recently reported by Stevenson et al. (2006), based on 25 chemical transport models. Our values also compare well with those of Grewe (2006) who obtained 420 Tg yr^{-1} and

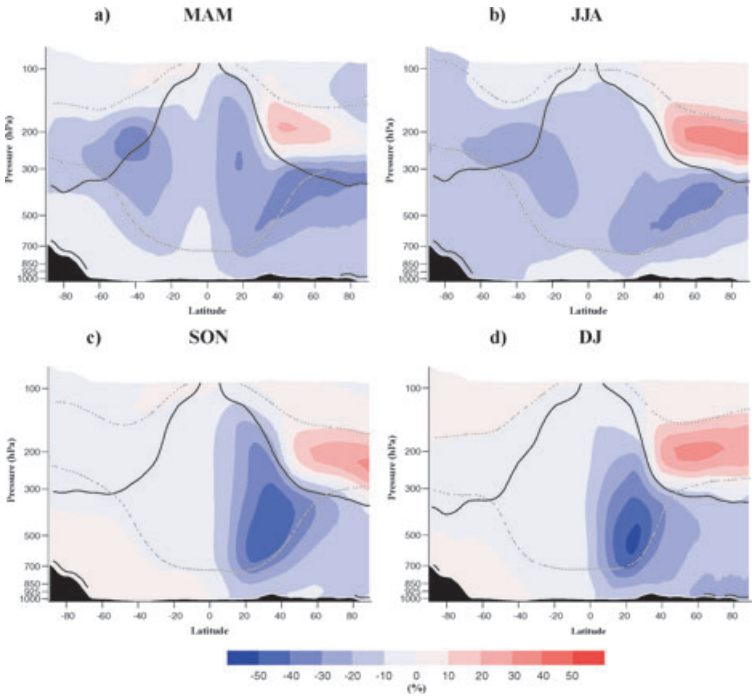

Fig. 9. Difference (%) between zonal means before and after assimilation of MOZAIC ozone data for each season, (a) MAM, (b) JJA, (c) SON and (d) DJ. The black line represents potential vorticity of ±2 PVU, that is, the tropopause, and the dashed lines are 310 K (lower) and 380 K (upper) isentropes.

who also used a method based on the Wei equation with pressure as vertical coordinate. He quoted a difference of around 10–20% between the Wei method compared with Lagrangian techniques for fluxes in DJF. Such a spread in values is partly explained by the wide variety of methods employed and the range of altitudes taken as the tropopause. Further reasons for the difference may be related to interannual variability which will be investigated using multiyear simulations with the model.

5. Conclusions

In this paper, we used the chemical transport model MOCAGE to calculate the flux of ozone across the tropopause. Ozone data from the MOZAIC project was assimilated into the model to improve the modelled ozone fields. The success of the assimilation was judged through comparisons with dependent and independent data sets. The assimilation increased the correlation between the dependent observations and the modelled ozone particularly in JJA when the model finds it harder to represent the impact of deep continental convection on the chemical distribution. The assimilation tended to reduce the tropical values of ozone which were overestimated in the model, and increased the concentrations in mid-latitudes which were underestimated by the model. The tropical–subtropical gradient was thus improved. Comparisons with ozonesonde profiles, which were independent of the assimilation, also suggested that the gradient of ozone around the tropopause was reinforced following the assimilation by increasing the concentration of ozone in the lower stratosphere and decreasing the concentration in the upper troposphere. The model still has difficulties in representing the gradients of ozone in the southern hemisphere at locations more remote from the MOZAIC network. This was evident in vertical profiles, and likely contributed to the unexpectedly higher flux in the southern hemisphere compared with that in the northern hemisphere. Assimilation of other data sources with coverage in the southern hemisphere and over the Pacific will be considered as a way of overcoming this problem.

The flux of ozone was calculated following the equation of Wei (1987) with geometric height as vertical coordinate and with the tropopause approximated as 2 PVU in mid-latitudes or the 380 K surface in the tropics. We calculated the magnitude of the net ozone flux of 451 Tg yr^{-1} without assimilation and 383 Tg yr^{-1} after the assimilation. Although there is some debate over the accuracy of this method, these values fall within the reported range, spanning a variety of different methods, tropopause heights, models and observations. Our values compare favourably to the 420 Tg yr^{-1} calculated by Grewe (2006) who used the Wei equation and the same choice of vertical coordinate. According to Grewe (2006), an uncertainty of 10–20% can be associated with values calculated by the Wei equation compared with those calculated by other methods.

Interannual variability may also account for differences between our values and other reported values but its effects have not been widely investigated. This is an important area of future research and this work will be extended by looking at multiyear simulations in which the interannual variability can be studied. The MOZAIC data are very useful in this respect offering a stable and consistent data set over more than a decade. The method of data assimilation used here is ideally suited to in situ measurements of ozone made from an aircraft platform and can be

adapted in the future to account for new routings that become available as MOZAIC operations continue under the IAGOS[1] project. It is hoped that about 20 aircraft will be equipped with MOZAIC-style sensors which will be operated by a variety of airlines giving coverage in the southern hemisphere and over the Pacific. The method can also take account of real-time data which will be assimilated in MOCAGE to improve the operational chemical weather forecasts.[2]

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