Atmos. Chem. Phys. Discuss., 12, 12023–12050, 2012
www.atmos-chem-phys-discuss.net/12/12023/2012/
doi:10.5194/acpd-12-12023-2012

Atmospheric Chemistry and Physics Discussions

Impact of meteorological analyses and chemical data assimilation on modelled long-term changes in stratospheric NO_2

L. N. Gunn[1,*], M. P. Chipperfield[1], W. Feng[1], M. Van Roozendael[2], M. Gil[3], M. Yela[3], P. V. Johnston[4], K. Kreher[4], and S. W. Wood[4,]**

[1]Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Leeds, UK
[2]Belgian Institute for Space Aeronomy, Brussels, Belgium
[3]Instituto Nacional de Técnica Aeroespacial, Spain
[4]NIWA, Lauder, New Zealand
[*]now at: Earth and Planetary Sciences, UC Berkeley, California, USA
[**]now at: 1981 Omakau-Chatto Creek Road, Alexandra, New Zealand

Received: 24 April 2012 – Accepted: 26 April 2012 – Published: 9 May 2012

Correspondence to: L. N. Gunn (lara.n.gunn@berkeley.edu)

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

Abstract

We have used a three-dimensional (3-D) off-line chemical transport model (CTM) to investigate long-term changes in stratospheric NO_2. The basic model was integrated from 1977 to 2001 using ECMWF (European Centre for Medium-Range Weather Forecasts) ERA-40 reanalyses. Additional model runs were performed which assimilated HALOE observations of long-lived tracers to constrain the model trace gas distributions. Assimilation of a single long-lived species (CH_4) improves not only the distribution of all other long-lived species, via tracer-tracer correlations, but also shorter lived radical and reservoir species. Assimilation of the long-lived species corrects for errors in the model, due to horizontal transport from the ERA-40 reanalyses, and allows a more direct test of the model's chemistry.

The basic model significantly underestimates the observed column NO_2 from mid-latitude ground-based sites in the mid-late 1990s. The mean underestimate is ~26 % for summertime values between 1992 and 1998. Moreover, as the model agreement is better in the early 1990s, it underestimates the increasing trend throughout the decade. However, when the model assimilates HALOE CH_4 data both comparisons are greatly improved. The mean model-observation difference reduces to 8 % for summertime values and the trend improves. This indicates that given realistic wind fields to constrain the tracer transport, the model chemistry and aerosol schemes are able to reproduce the observed trends in NO_2.

Implications of this for using analysed wind fields to determine dynamical ozone trends are discussed. Ozone trends derived directly from transport models forced by analysed winds are likely subject to similar errors.

1 Introduction

Nitrogen dioxide (NO_2) plays a key role in stratospheric chemistry. It is directly involved in the major stratospheric odd-oxygen loss cycle and it also interacts with other key

ACPD
12, 12023–12050, 2012

species in the odd-hydrogen, chlorine and bromine families. It is therefore important to observe its distribution and long-term changes and to be able to simulate these changes accurately in global chemistry models.

The longest records of stratospheric NO_2 have been obtained from ground-based observations. Liley et al. (2000) presented results from the early 1980s until 2000 at Lauder, New Zealand (45° S) which showed overall increases of around $5 \pm 1\,\%\,\text{decade}^{-1}$. WMO (2006) updated these Lauder trends through 2006 and obtained values of $6.2 \pm 1.8\,\%\,\text{decade}^{-1}$ sunrise (a.m.) and $5.7 \pm 1.1\,\%\,\text{decade}^{-1}$ sunset (p.m.). WMO (2006) also derived trends from IR absorption studies of midday column NO_2 (Mahieu et al., 2000) from the Jungfraujoch (46.3° N) from 1985. For these data the equivalent analysis as the Lauder data gave a trend of only $1.5 \pm 1.0\,\%\,\text{decade}^{-1}$. Therefore, the observed trend in the Southern Hemisphere appears significantly larger than in the Northern Hemisphere.

The source of stratospheric NO_y, and therefore NO_2, is N_2O. Tropospheric N_2O increased at a rate of $2.4\,\%\,\text{decade}^{-1}$ from 1986–2005 (WMO, 2011). Fish et al. (2000) and McLinden et al. (2001) used photochemical models to analyse the observed NO_2 trend at Lauder. They concluded that the larger trend in NO_2 compared to N_2O could be largely accounted for by the impact of ozone depletion which contributed an additional $2.5\,\%\,\text{decade}^{-1}$.

Off-line 3-D models have been used to study long-term trends and variability in stratospheric ozone. These studies make use of the availability of reanalysis data sets such as the ECMWF (European Centre for Medium-Range Weather Forcasts) ERA-40 (Uppala et al., 2005) or ERA-Interim (Dee et al., 2011). Feng et al. (2007) used the SLIMCAT 3-D CTM and ERA-40 reanalyses to study changes in mid-latitude stratospheric ozone from 1977–2004. Their study mainly focused on the role of increasing halogens on ozone trends but they noted that errors in the analysed winds used to force the model caused apparently spurious variations in model chemical species. While the CTM could still be used for chemical experiments, these variations really seemed to preclude the use of the analyses to derive long-term dynamical trends.

ACPD
12, 12023–12050, 2012

Chemical data assimilation has been increasingly used over the past 20 years as a means of using atmospheric observations to formally constrain models. Early studies included the work of Fisher and Lary (1995) who used a box model with a simplified photochemical scheme and assimilated observations along trajectories. Subsequent 3-D model studies included Levelt et al. (1998), who used a Kalman filter approach, and Errera and Fonteyn (2001) who used a variational method. Chemical data assimilation is now employed routinely at meteorological forecasting centres such as the ECMWF (Dethof, 2003).

Gil et al. (2008) presented observations of column NO_2 from the subtropical site of Tenerife (28° N, 344° E) from 1993 to 2006. Their study included comparisons of the mean annual cycle in column NO_2 with mean results from SLIMCAT simulations from 1996–2000. They found that the basic model, forced by ERA-40 meteorology but with free-running chemistry, underestimated the observed column by up to 12 % at sunrise and 25 % at sunset. However, they found that by assimilating stratospheric CH_4 observations into the model, to constrain the model long-lived tracer distributions, they got much better agreement with the observations at this site over the mean annual cycle.

This paper investigates the modelled long-term trend in stratospheric column NO_2 at a range of mid-latitude and subtropical sites. As in Gil et al. (2008) we use the SLIMCAT 3-D CTM in both chemically free running and data assimilation modes. We extend on the observation-based study of Gil et al. (2008) by analysing the modelled trends over the period 1992–2002, by studying a range of stations and by investigating the cause of the model improvements when assimilation of a long-lived tracer is included.

Section 2 describes the model and experiments. Section 3 discusses the model results and Sect. 4 summarises our conclusions.

ACPD
12, 12023–12050, 2012

2 Model and experiments

2.1 SLIMCAT 3-D CTM

SLIMCAT is an off-line 3-D CTM described in detail by Chipperfield (1999). The model has been used in many past studies of stratospheric chemistry and has been shown to perform well at simulating key chemistry and transport processes. The model uses a hybrid σ-θ vertical coordinate (Chipperfield, 2006) and extends from the surface to a top level which depends on the domain of the forcing analyses. Vertical advection in the θ-level domain is calculated from diabatic heating rates using a radiation scheme which gives a better representation of vertical transport and age-of-air even with ERA-40 reanalyses (Chipperfield, 2006). The model contains a detailed stratospheric chemistry scheme including a treatment of heterogeneous reactions on liquid aerosols, nitric acid trihydrate (NAT) and ice (Chipperfield, 1999). The current details of the chemistry scheme are as described in Feng et al. (2005, 2011).

2.2 Model experiments

In the experiments described here the 3-D model was run with 32 levels from the surface to approximately 60 km at two different model resolutions, $5.6^\circ \times 5.6^\circ$ and $2.8^\circ \times 2.8^\circ$. The model was forced using the 6-hourly 60-level ECMWF (re)analyses. From 1 January 1977 to 31 December 2001 we have used the standard ERA-40 product (Uppala et al., 2005). After this date we have used the operational analyses which are subject to periodic update. Time-dependent monthly fields of liquid sulfate aerosol for 1979–1999 were taken from WMO (2002). When the model simulations extended beyond 1999 the aerosol was kept constant at the 1999 values. The time-dependent surface mixing ratios of source gases were also taken from WMO (2002).

Strahan and Polansky (2006) discussed the resolution required in their CTM in order to give an accurate representation of stratospheric tracer transport. They concluded that a realistic representation of transport barriers requires a model grid of 2°

ACPD
12, 12023–12050, 2012

latitude × 2.5° longitude. However, these values are likely to be model-dependent. Modelled tracer distributions will be affected by the advection scheme used. In SLIMCAT we use the Prather (1986) scheme which conserves second-order moments and has low numerical diffusion. As the model is formulated on isentropic levels in the stratosphere this also gives a clearer separation of vertical and horizontal tracer transport which reduces tracer mixing. Our CTM also averages the ECMWF analyses (available as spectral coefficients) onto the particular model grid used in a method which reduces noise that can occur when interpolating grid point winds. For these reasons we find that SLIMCAT can give a reasonable representation of stratospheric tracers at resolutions lower than 2° × 2.5°. Nevertheless, in this study we also investigate the impact of model resolution.

The model was initialised on 1 January 1977 using output from a 2-D model and integrated until the end of 2001 in a series of experiments (see Table 1). Run A used the basic model at a model resolution of 5.6° × 5.6°. Run B was performed from 1991 and was the same as run A but included assimilation of chemical data using the method described in Chipperfield (2003).

The SLIMCAT assimilation scheme uses a sub-optimal Kalman filter (a sequential assimilation scheme), previously described by Khattatov et al. (2000). The scheme uses observations from the HALOE instrument (Russell et al., 1993), from which four long-lived chemical species are used; O_3 (Bruehl et al., 1996), HCl (Russel et al., 1996), H_2O (Harries et al., 1996), and CH_4 (Park et al., 1996) (all version 19). These data are available on ∼ 15 sunrise/sunset profiles per day. The latitude of these HALOE observations varies over the course of a couple of months.

The main effect of sequential chemical data assimilation on the SLIMCAT model is to correct for any model transport errors. As all tracers in the model are overwritten at the surface and advected into the stratosphere, problems with transport will cause the distribution of tracers to be wrong, e.g. incorrect age-of-air.

There are key constraints within SLIMCAT to allow the assimilation of 4 long-lived tracers to impact all chemical species in SLIMCAT. The first constraint is on the

ACPD
12, 12023–12050, 2012

modelled long-lived tracers. Plumb and Ko (1992) showed that there are compact correlations between the mixing ratios of long-lived tracers in the stratosphere. As shown in Chipperfield et al. (2002), these relationships can be used to constrain the model allowing the assimilated tracers to impact all the other long-lived tracers in the model.

Another key constraint is on HCl. It is known from measurements of atmospheric halocarbons concentrations, e.g. Chlorofluorocarbons (CFCs), that there is a limit on Cl_y of around 3.6 ppbv for 1990 conditions (WMO, 2006). Therefore, assimilated HCl is constrained so that its value does not exceed that expected from the modelled Cl_y. As all long-lived tracers are constrained either through assimilation or tracer-tracer correlations, the shorter lived species are simply affected through the model chemistry.

Run C was the same as run B but without assimilation of O_3. This allows us to investigate the impact of ozone changes on NO_x partitioning. Run D was the same as run A but at a higher resolution ($2.8^\circ \times 2.8^\circ$). This is to investigate the impact of other possible sources of transport error related to the moderate resolution of the basic model.

3 Results

Section 3.1 compares the model runs with independent observations and assesses the model improvements in relevant trace species after chemical data assimilation. Section 3.2 investigates the impact of assimilation on the long-term variation of model tracers. Section 3.3 discusses what the model runs show for the long-term trends in column NO_2. Finally, Sect. 3.4 discusses what these model results imply for the use of off-line CTM's in investigating long-term trends in ozone.

3.1 Comparison with independent observations

Figure 1 shows comparisons of long-lived tracers, HCl and O_3 from the 3 low resolution model runs with ATMOS observations in November 1994. While the modelled CH_4 and

ACPD
12, 12023–12050, 2012

H_2O profiles from run A are reasonable, the assimilation of the HALOE data improves the model–observation fit. Although it is not assimilated, the preservation of the model long-lived tracer-tracer correlations (Chipperfield et al., 2002) means that in runs B and C the model N_2O profile is also in much better agreement with the ATMOS data. Below about 30 hPa, where O_3 is relatively long-lived, run B, which assimilates O_3, agrees better with the ATMOS data. Above this altitude the short lifetime of O_3 means that there is essentially no direct impact of assimilating it.

Figure 2 shows comparisons of shorter lived species from the model runs with ATMOS data. None of these species is directly assimilated. The assimilation process can affect their distribution by modifying the abundance of the long-lived total families NO_y and Cl_y through the tracer-tracer correlations (as in N_2O and CH_4 in Fig. 1). For NO and NO_2 below ~ 10 hPa, the assimilation runs B and C show improved agreement with the ATMOS profiles. This is the region which will be most important for the column contributions. For HNO_3, the most abundant NO_y reservoir species in the lower stratosphere, the profile comparison is again improved in runs B and C through improvements in the NO_y profile.

Figure 3 shows comparisons of column HNO_3 from 4 ground-based stations during 1997 and 1998. Column HNO_3 is the largest component of column NO_y in the stratosphere and so an indicator of modelled changes in this long-lived tracer. At all the stations the assimilation runs have larger column HNO_3, consistent with the "descent" seen in the N_2O profiles in Fig. 1. This leads to improved comparisons with the observations at all sites with a marked improvement at Lauder and Arrival Heights. Overall the assimilation of long-lived tracers has improved the column comparison for this key NO_y species.

3.2 Long-term variations

Figure 4 shows the timeseries of model CH_4 at 56 hPa (~ 20 km) and 3.2 hPa (~ 40 km) averaged over the Northern and Southern Hemisphere mid-latitudes. The differences in the model runs are only apparent after the assimilation of HALOE data begins in 1992.

ACPD
12, 12023–12050, 2012

Also shown in Fig. 4 is the HALOE v19 monthly mean satellite data averaged over this same region. The small differences between run B (and run C which is essentially identical and not shown) and the observations are due to the data being assimilated profile by profile at the specific time of observation, while the plot shows a simple average of HALOE data, and the fact that the assimilation scheme considers errors in the observation and model before producing a best "analysis". For this long-lived tracer, variations in the model timeseries in run A reflect changes in the model transport which in turn come from the forcing ECMWF analyses. As discussed in Feng et al. (2007), some of this dynamical variability may be real while some may result from changes to the Numerical Weather Prediction (NWP) assimilation system or changes to the data being assimilated by it. The long-term variation produced by the model and ERA-40 analyses from, say, 1992–2002, is not realistic. In contrast, assimilating CH_4 constrains the model to have a realistic trend in this species, albeit with a large jump when assimilation starts.

Figure 5 is a similar plot comparing the model with the assimilated HALOE H_2O. Again run A shows significant differences with respect to the observations which indicate an unrealistic long-term trend.

3.3 Long-term NO_2 variations

Having shown that long-term chemical data assimilation in the model can improve the modelled distribution of key NO_y species, and correct for transport errors, we now investigate the implications for long-term modelled NO_2 variations. Figures 6 and 7 show the comparison of modelled sunrise and sunset column NO_2 for 1992–2000 from 4 stations: Jungfraujoch, Issyk-Kul, Tenerife and Lauder. The data were obtained as part of the Network for the Detection of Atmospheric Composition Change (NDACC, http://www.ndacc.org). The observations are characterised by an annual cycle (larger at midlatitudes) and an increasing trend. This increasing trend is due both to increasing stratospheric NO_y due to increasing N_2O and decreasing aerosol following the eruption

ACPD
12, 12023–12050, 2012

of Mt Pinatubo in 1991. As noted in the introduction, there is also a contribution from the effect of decreasing ozone (Fish et al., 2000; McLinden et al., 2001).

The comparison of the basic model run A with the observations is quite poor especially in the late 1990s. The model captures the annual cycle but significantly underestimates the magnitude of the summertime maximum (e.g. by ∼26 % averaged over all stations). Column NO_2 in run A does increase during this period but not by as much as in the observations. Evidently this modelled NO_2 trend in run A is therefore too small.

Both of the moderate resolution model runs which include chemical data assimilation show much better agreement throughout the whole period shown. The improvement is especially marked in the late 1990s. The modelled summertime maximum is now in good agreement with the observations (e.g. an underestimation of ∼8 %). Moreover, the modelled NO_2 trend over this period agrees with the observations. Note the improvement in modelled NO_2 in runs B and C is due to improvements in the modelled distribution of NO_y via its correlation with the long-lived tracer CH_4. The chemical partitioning of NO_y, and indeed the production of NO_y from N_2O is still determined by the model chemistry. Therefore, the NO_2 comparison is still testing many aspects of the model.

The improved agreement in the modelled NO_2 column following data assimilation is quantified in Table 2. Averaged over all observation times between 1992 and 2000 run A underestimates the measurements at Jungfraujoch, Issyk-Kul and Lauder. At Tenerife run A overestimates the observations due to an overestimate in winter not capturing the timing of the annual cycle at this sub-tropical station. Except for Tenerife, following data assimilation the observation-model difference decreases significantly. At Jungfraujoch the difference decreases from 19 %/22 % in run A to −7 %/−1 % in run B and −1 %/+2 % in run C. The agreement at Issyk-Kul also improves considerably but the model agreement is not as good as at Jungfraujoch. While the model shows similar values at these two stations, which are at similar latitudes, the observations at Issyk-Kul are larger than at Jungfraujoch.

ACPD
12, 12023–12050, 2012

Figures 6 and 7 also include the high resolution run D. This was only run for the beginning of the 1990s, but it can be seen that the higher resolution does not make any significant improvements to the model agreement with the observations. While chemical data assimilation could correct for a range of transport errors, the results from run D indicate that the main source of transport error in run A is not due to its resolution, but a consequence of the information in the analysed winds.

The difference in column NO_2 between runs B and C is small. This indicates that the impact of changing model O_3 through assimilation is not a significant cause of the model improvement. The concentration of O_3 does affect the daytime NO_2 abundance, i.e. via the $[NO]:[NO_2]$ partitioning. However, the ozone field from the free-running model (run A) is realistic enough in the important altitude region (20–30 km) that any improvement via assimilation causes only a small change to column NO_2.

The nighttime conversion of NO_2 to N_2O_5 is determined by the following reactions:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (1)$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \quad (2)$$

N_2O_5 itself can thermally decompose to reform NO_2 + NO_3:

$$N_2O_5 + M \rightarrow NO_3 + NO_2 + M \quad (3)$$

If the rate of Eq. (2) is fast at night, and Eq. (3) is not important, we can place nighttime NO_3 in steady state and the rate of loss of NO_2 becomes:

$$\frac{-\mathrm{d}[NO_2]}{\mathrm{d}t} = -2k_1[NO_2][O_3]$$

so the overall decay of NO_2 between sunset and sunrise is:

$$[NO_2]_{sr} = [NO_2]_{ss} \exp(-2k_1[NO_2][O_3])$$

Therefore, the ratio of sunset : sunrise NO_2 is determined by atmospheric temperature (via k_1) and the concentration of O_3. Figure 8 shows the observed ratio of column

ACPD
12, 12023–12050, 2012

sunset : sunrise NO_2 for 4 stations from 1997–1998, along with results from the 3 model runs. The observations show a sunset : sunrise column ratio of about 1.0–2.0. There is an apparent annual cycle in the ratio at Lauder with highest values in late winter/spring. This could be associated with low ozone and cold temperatures associated with high latitude ozone loss. Smaller variations are seen at Jungfraujoch. At Tenerife there is an apparent annual cycle with larger ratios in late autumn/winter. The observed ratio at Issyk-Kul shows high variability, with large ratios in winter. The model shows less variability in the sunset : sunrise column ratio than the observations. It does capture the annual cycle at Lauder but misses the enhanced values at Tenerife and Issyk-Kul. The modelled ratio is very similar between runs A and C. All model runs used the same temperature fields and the O_3 fields in these 2 runs in the altitude region important for the NO_2 column are also similar. The modelled ratio from run B, which assimilates ozone, is slightly smaller. However, this does not impact the agreement with the observations. The overall fair long-term agreement between the model and observations, however, indicates that this aspect of NO_2 chemistry, i.e. the nighttime decay, is well modelled. This supports the argument that the improvements seen in model column NO_2 in Figs. 6 and 7 is due to changes in NO_y, and not a chemical effect.

An important result from Figs. 6 and 7 is the implication for the cause of the modelled NO_2 trend. Given the poor agreement of run A it would have been tempting to question whether the modelled aerosol trend was realistic. However, runs B and C use the same aerosol values and can reproduce the observations. Overall the results point to the cause of the poor agreement in run A being principally due to the transport related errors in the forcing ERA-40 winds.

3.4 Ozone

Analysed wind fields are used to quantify the role of dynamics in long-term changes in column ozone (WMO, 2006, 2011). This can be via their use to force long-term CTM simulations or via direct diagnosis of dynamical quantities. The results presented here add a further note of caution to the process of taking long-term reanalysis datasets and

ACPD
12, 12023–12050, 2012

using them to derive trends. Even when created with a constant assimilation system, the reanalyses may have discontinuities when different datasets become available for assimilation.

More specifically, the results presented here show that the modelled midlatitude ozone trends from the basic model would not be realistic in the 1990s. Feng et al. (2007) presented long-term ozone variations from a run very similar to run A. The long-term ozone change was expressed as a percentage anomaly relative to 1980 (their Fig. 4). While the model captured the overall long-term change from 1980–2002 there were periods where the model disagreed significantly, e.g. an overestimate in the late 1980s and an underestimate in the early 1990s. Indeed, Fig. 4 of Feng et al. (2007) shows that model run A has a too strong increase in column ozone from 1993 to around 1998. As we are now able to assimilate a long-lived tracer from 1991 onwards, we can interpret this underestimate of O_3 in the early 1990s as being due, at least in part, to errors in the long-term variations in ERA-40 analyses. Unfortunately, we cannot repeat the "anomaly" analysis of Feng et al. (2007) as we do not have observations to constrain the assimilation runs back to 1980.

4 Conclusions

We have used the SLIMCAT off-line 3-D chemical transport model to investigate long-term changes in stratospheric nitrogen dioxide in the mid-latitude lower and upper stratosphere. The CTM was forced using ECMWF ERA-40 reanalyses from 1977 until the end of 2001. Further model experiments used the assimilation of a long-lived tracer to constrain the model chemical fields. The assimilation of this single long-lived species (CH_4) improves not only the distribution of all other long-lived species, via tracer-tracer correlations, but also shorter lived radical and reservoir species.

The basic model significantly underestimates the observed column NO_2 from mid-latitude ground-based sites before about 1998. The mean underestimate is around 26 % for summertime values between 1992 and 1998. Moreover, as the model

ACPD
12, 12023–12050, 2012

agreement is worse in the late 1990s, it underestimates the increasing trend later in the decade. However, when the model assimilates HALOE CH_4 data both comparisons are greatly improved. The mean model-observation difference at northern mid-latitudes is now only 8 % for summertime values between 1992 and 1998. Results from a higher resolution model show very similar results to the basic non-assimilation models. This shows that the transport errors in the model cannot be improved simply by increasing the resolution but are more fundamentally linked to the information contained in the winds used to force the model.

These results have implications for the use of analysed winds in determining the dynamical contribution to column ozone changes, especially when using them to force a transport model. Clearly, modelled column ozone changes will be sensitive to errors in the analysed winds. Unfortunately, the availability of long-lived tracer data for assimilation does not extend over the long period typically used for stratospheric ozone trend studies (e.g. 1980 to present day).

Assimilation of the long-lived species corrects for transport errors in the model (i.e. from the ERA-40 reanalyses) and allows a more direct test of the model's chemistry. With this constraint, it appears that our current understanding of atmospheric chemistry can then quantitatively reproduce observed long-term column NO_2 changes. However, the period over which this study can be performed is limited by the availability of suitable tracer observations to assimilate. This study shows that long-term, continuous, global, height-resolved observations of at least one long-lived tracer would be a very useful constraint on 3-D CTM studies and can effectively correct for model transport errors.

Acknowledgements. This work was supported by the UK Natural Environment Research Council (NCEO) and by the EU through the SCOUT-O3 and GEOMON projects. LNG thanks the NERC Data Assimilation Research Centre (DARC) for a studentship. We acknowledge use of the ATMOS and HALOE data. Ground-based data used in this paper was obtained as part of the Network for the Detection of Atmospheric Composition Change (NDACC) and is publicly available (see http://www.ndacc.org). We acknowledge Dan Smale and John P. Robinson (HNO_3 measurements) and Alan J. Thomas (NO_2 measurements). WF is partly funded my NCAS.

ACPD
12, 12023–12050, 2012

References

Bruehl, C., Drayson, S. R., Russel III, J. M., Crutzen, P. J., McInerney, J. M., Purcell, P. N., Claude, H., Gernandt, H., McGee, T. J., McDermid, I. S., and Gunson, M. R.: Halogen occultation experiment ozone channel validation, J. Geophys. Res., 101, 10217–10240, doi:10.1029/95JD02031, 1996. 12028

Chipperfield, M. P.: Multiannual simulations with a three-dimensional chemical transport model, J. Geophys. Res., 104, 1781–1805, doi:10.1029/98JD02597, 1999. 12027

Chipperfield, M. P.: A three-dimensional model study of long-term mid-high latitude lower stratosphere ozone changes, Atmos. Chem. Phys., 3, 1253–1265, doi:10.5194/acp-3-1253-2003, 2003. 12028

Chipperfield, M. P.: A new version of the TOMCAT/SLIMCAT off-line chemical transport model: intercomparison of stratospheric tracer experiments, Q. J. Roy. Meteor. Soc., 132, 1179–1203, doi:10.1256/qj.05.51, 2006. 12027

Chipperfield, M. P. and Jones, R. L.: Relative influences of atmospheric chemistry and transport on Arctic O_3 trends, Nature, 400, 551–554, 1999.

Chipperfield, M. P., Khattatov, B. V., and Lary, D. J.: Sequential assimilation of stratospheric chemical observations in a three-dimensional model, J. Geophys. Res., 107, 4585, doi:10.1029/2002JD002110, 2002. 12029, 12030

Chipperfield, M. P., Feng, W., and Rex, M.: Arctic ozone loss and climate sensitivity: updated three-dimensional model study, Geophys. Res. Lett., 32, L11813, doi:10.1029/2005GL022674, 2005.

Dee, D. P., Uppala S. M., Simmons A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Holm, E. V., Isaksen, L., Kallberg, P., Koehler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park, B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N., and Vitart, F.: The ERA-interim reanalysis: configuration and performance of the data assimilation system, Q. J. Roy. Meteor. Soc., 137, 553–597, doi:10.1002/qj.828, 2011. 12025

Dethof, A. E.: Assimilation of ozone retrievals from the MIPAS instrument onboard ENVISAT, ECMWF Tech Memo 428, ECMWF, available at: http://www.ecmwf.int/publications, 2003. 12026

ACPD
12, 12023–12050, 2012

Errera, Q. and Fonteyn, D.: Four-dimensional variational chemical assimilation of CRISTA stratospheric measurements, J. Geophys. Res., 106, 12253–12265, 2001. 12026

Feng, W., Chipperfield, M. P., Davies, S., Sen, B., Toon, G., Blavier, J. F., Webster, C. R., Volk, C. M., Ulanovsky, A., Ravegnani, F., von der Gathen, P., Jost, H., Richard, E. C., and Claude, H.: Three-dimensional model study of the Arctic ozone loss in 2002/2003 and comparison with 1999/2000 and 2003/2004, Atmos. Chem. Phys., 5, 139–152, doi:10.5194/acp-5-139-2005, 2005. 12027

Feng, W., Chipperfield, M. P., Dorf, M., Pfeilsticker, K., and Ricaud, P.: Mid-latitude ozone changes: studies with a 3-D CTM forced by ERA-40 analyses, Atmos. Chem. Phys., 7, 2357–2369, doi:10.5194/acp-7-2357-2007, 2007. 12025, 12031, 12035

Feng, W., Chipperfield, M. P., Davies, S., Mann, G. W., Carslaw, K. S., Dhomse, S., Harvey, L., Randall, C., and Santee, M. L.: Modelling the effect of denitrification on polar ozone depletion for Arctic winter 2004/2005, Atmos. Chem. Phys., 11, 6559–6573, doi:10.5194/acp-11-6559-2011, 2011. 12027

Fish, D. J., Roscoe, H. K., and Johnston, P. V.: Possible causes of stratospheric NO_2 trends observed at Lauder, New Zealand, Geophys. Res. Lett., 27, 3313–3316, doi:10.1029/2000GL011700, 2000. 12025, 12032

Fisher, M. and Lary, J. D.: Lagrangian 4-dimensional variational data assimilation of chemical species, Q. J. Roy. Meteor. Soc., 121, 1681–1704, 1995. 12026

Gil, M., Yela, M., Gunn, L. N., Richter, A., Alonso, I., Chipperfield, M. P., Cuevas, E., Iglesias, J., Navarro, M., Puentedura, O., and Rodríguez, S.: NO_2 climatology in the northern subtropical region: diurnal, seasonal and interannual variability, Atmos. Chem. Phys., 8, 1635–1648, doi:10.5194/acp-8-1635-2008, 2008. 12026

Hadjinicolaou, P., Jrrar, A., Pyle, J. A., and Bishop, L.: The dynamically driven long-term trend in stratospheric ozone over northern mid-latitudes, Q. J. Roy. Meteor. Soc., 128, 1393–1412, 2002.

Hadjinicolaou, P., Pyle, J. A., and Harris, N. R. P.: The recent turnaround in stratospheric ozone over northern middle latitudes: a dynamical modelling perspective, Geophys. Res. Lett., 32, L12821, doi:10.1029/2005GL022476, 2005.

Harries, J. E., Russell, J. M., Tuck, A. F., Gordley, L. L., Purcell, P., Stone, K., Bevilacqua, R. M., Gunson, M., Nedoluha, G., and Traub, W. A.: Validation of measurements of water vapor from the Halogen Occultation Experiment (HALOE), J. Geophys. Res., 101, 10205–10216, 1996. 12028

ACPD
12, 12023–12050, 2012

Khattatov, B. V., Lamarque, J. F., Lyjak, L. V., Menard, R., Levelt, P., Tie, X., Brasseur, G. P., Gille, J. C.: Assimilation of satellite observations of long-lived chemical species in global chemistry transport models, J. Geophys. Res., 105, 29135–29144, 2000. 12028

Levelt, P. F., Khattatov, B. V., Gille, J. C., Brasseur, G. P., Tie, X. X., and Waters, J. W.: Assimilation of MLS ozone measurements in the global three-dimensional chemistry transport model ROSE, Geophys. Res. Lett., 25, 4493–4496, 1998. 12026

Liley, J. B., Johnston, P. V., Mackenzie, R. L., Thomas, A. J., and Boyd, I. S.: Stratospheric NO_2 variations from a long time series at Lauder, New Zealand, J. Geophys. Res., 105, 11633–11640, 2000. 12025

Mahieu, E., Zander, R., Mélen, F., Demoulin, P., Rinsland, C. P., and Russel III, J. M.: Monitoring the stratospheric chlorine budget during the past decades: the Montreal Protocol at work, in: Proceedings of the "International Quadrennial Ozone Symposium", Sapporo, Japan, 3–8 July 2000, 149–150, 2000. 12025

McLinden, C. A., Olsen, S. C., Prather, M. J., and Liley J. B.: Understanding trends in NO_y and NO_2, J. Geophys. Res., 106, 27787–27793, 2001. 12025, 12032

Park, J. H., Russell III, J. M., Gordley, L. L., Drayson, S. R., Benner, D. C., McInerney, J. M., Gunson, M. R., Toon, G. C., Sen, B., Blavier, J.-F., Webster, C. R., Zipf, E. C., Erdman, P., Schmidt, U., and Schiller, C.: Validation of Halogen Occultation Experiment CH_4 measurements from the UARS, J. Geophys. Res., 101, 10217–10240, 1996. 12028

Plumb, R. A. and Ko, M. K. W.: Interrelationships between mixing ratios of long-lived stratospheric constituents, J. Geophys. Res., 97, 10145–10156, 1992. 12029

Prather, M. J.: Numerical advection by conservation of second-order moments, J. Geophys. Res., 91, 6671–6681, 1986. 12028

Russell III, J. M., Gordley, L. L., Park, J. H., Drayson, S. R., Hesketh, D. H., Cicerone, R. J., Tuck, A. F., Frederick, J. E., Harries, J. E., and Crutzen, P. J.: The Halogen Occultation Experiment, J. Geophys. Res., 98, 10777–10797, 1993. 12028

Russell III, J. M., Deaver, L. E., Luo, M., Park, J. H., Gordley, L. L., Tick, A. F., Toon, G. C., Gunson, M. R., Traub, W. A., Johnson, D. G., Jucks, K. W., Murcray, D. G., Zander, R., Nolt, I. G., and Webster, C. R.: Validation of hydrogen chloride measurements made by the Halogen Occultation Experiment from the UARS platform, J. Geophys. Res., 101, 10151–10162, 1996. 12028

Sinnhuber, B.-M., Arlander, D. W., Bovensmann, H., Burrows, J. P., Chipperfield, M. P., Enell, C.-F., Frieß, U., Hendrick, F., Johnston, P. V., Jones, R. L., Kreher, K., Mohamed-Tahrin, N.,

ACPD
12, 12023–12050, 2012

Müller R., Pfeilsticker, K., Platt, U., Pommereau, J.-P., Pundt, I., Richter, A., South, A. M., Tørnkvist, K. K., Van Roozendael, M., Wagner, T., and Wittrock, F.: Comparison of measurements and model calculations of stratospheric bromine monoxide, J. Geophys. Res., 107, D19, doi:10.1029/2001JD000940, 2002.

Strahan, S. E. and Polansky, B. C.: Meteorological implementation issues in chemistry and transport models, Atmos. Chem. Phys., 6, 2895–2910, doi:10.5194/acp-6-2895-2006, 2006. 12027

Uppala, S. M., Kallberg, P. W., Simmons, A. J., Andrae, U., Costa Bechtold, V., da Fiorino, M., Gibson, J. K., Haseler, J., Hernandez, A., Kelly, G. A., Li, X., Onogi, K., Saarinen, S., Sokka, N., Allan, R. P., Andersson, E., Arpe, K., Balmaseda, M. A., Beljaars, A. C. M., Van de Berg, L., Bidlot, J., Bormann, N., Caires, S., Chevallier, F., Dethof, A., Drafosavac, M., Fisher, M., Fuentes, M., Hagemann, S., Holm, E., Hoskins, B. J., Isaken, L., Janssen, P. A. E. M., Jenne, R., McNally, A. P., Mahfouf, J.-F., Morcrette, J-J., Rayner, N. A., Saunders, R. W., Simon, P., Sterl, A., Trenberth, K. E., Untch, A., Vasiljevis, D., Viterbo, P., and Woolen, J.: The ERA-40 re-analysis, Q. J. Roy. Meteor. Soc., 131, 2961–3012, doi:10.1256/qj.04.176, 2005. 12025, 12027

World Meteorological Organization (WMO): Scientific Understanding of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project – Report No. 47, World Meteorological Organization, Geneva, 2003. 12027

World Meteorological Organization (WMO): Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project – Report No. 50, World Meteorological Organization, Geneva, 2007. 12025, 12029, 12034

World Meteorological Organization (WMO): Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project – Report No. 52, World Meteorological Organization, Geneva, 2011. 12025, 12034

ACPD

12, 12023–12050, 2012

Table 1. SLIMCAT CTM experiments.

Run	Dates	Chemical assimilation	Resolution
A	1977–2002	None	5.6° × 5.6°
B	1991–2002	HALOE CH_4, H_2O, HCl, O_3	5.6° × 5.6°
C	1991–2002	HALOE CH_4, H_2O, HCl	5.6° × 5.6°
D	1991–1993	None	2.8° × 2.8°

ACPD
12, 12023–12050, 2012

Table 2. Mean percentage difference in column NO_2 between observations and SLIMCAT model runs from 1992–2000.

	Run A		Run B		Run C	
	Sunrise	Sunset	Sunrise	Sunset	Sunrise	Sunset
Jungfraujoch	19 %	22 %	−7 %	−1 %	−1 %	2 %
Issyk-Kul	45 %	48 %	4 %	21 %	11 %	25 %
Tenerife	−30 %	−11 %	−30 %	−29 %	−27 %	−28 %
Lauder	22 %	15 %	3 %	7 %	12 %	12 %

ACPD
12, 12023–12050, 2012

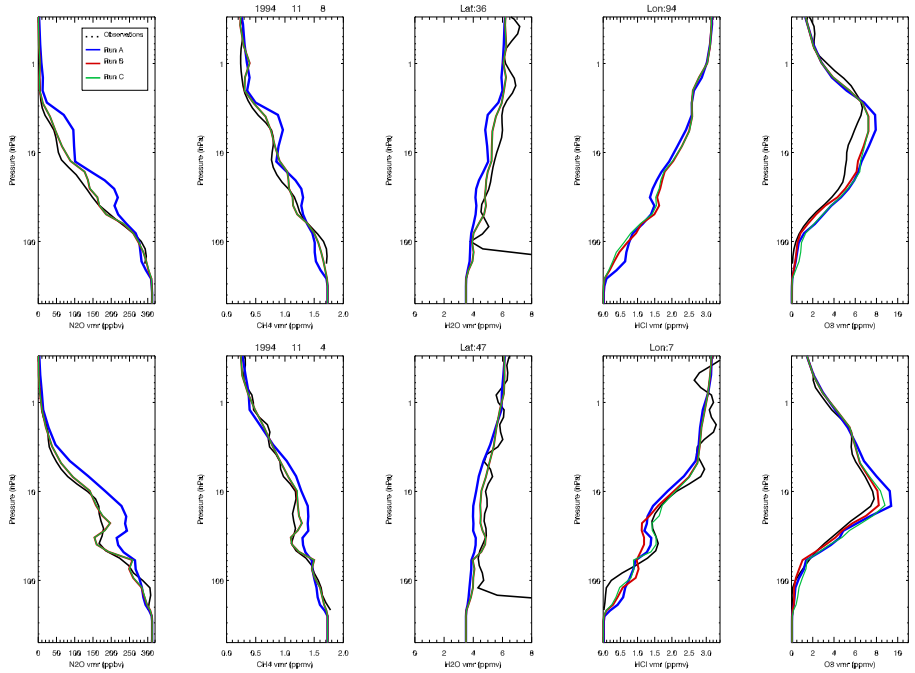

Fig. 1. Observed profiles (from left to right) of N_2O, CH_4, H_2O, HCl and O_3 from ATMOS on 8 November 1994 for 36.4° N, 93.8° E (top) and 47.6° N, 7.7° E (bottom). Also shown are model results from runs A (blue line), B (red line) and C (green line). For H2O only model stratospheric tracer values are shown. On the top panel there is no available ATMOS data for HCl.

ACPD
12, 12023–12050, 2012

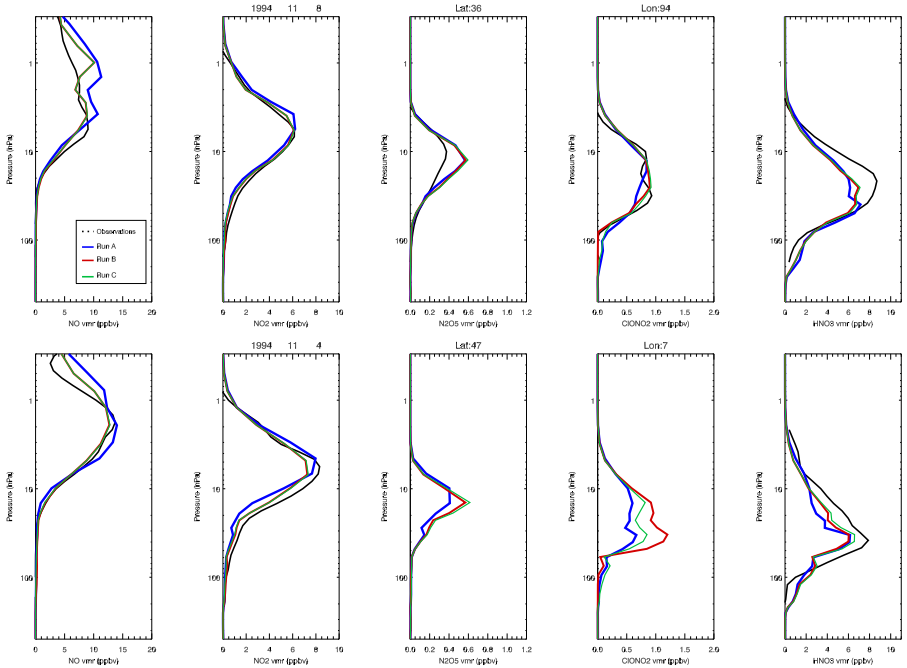

Fig. 2. As Fig. 1 but for (from left to right) NO, NO_2, N_2O_5, $ClONO_2$, and HNO_3.

ACPD
12, 12023–12050, 2012

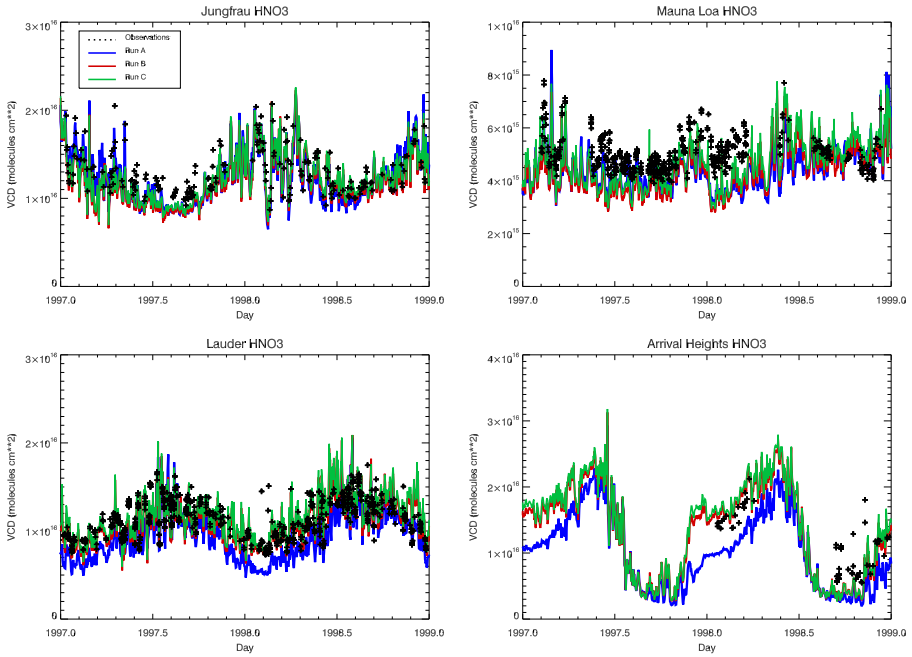

Fig. 3. Observed column HNO_3 (molecules cm^{-2}) for 1997–1999 (+ marks) at Jungfraujoch (46.346.3° N, 7.646.3° E), Mauna Loa (19.546.3° N, 156.046.3° W), Lauder (45.046.3° N, 169.746.3° E) and Arrival Heights (77.846.3° N, 166.746.3° E). Also shown are model results from runs A (blue line), B (red line) and C (green line).

ACPD
12, 12023–12050, 2012

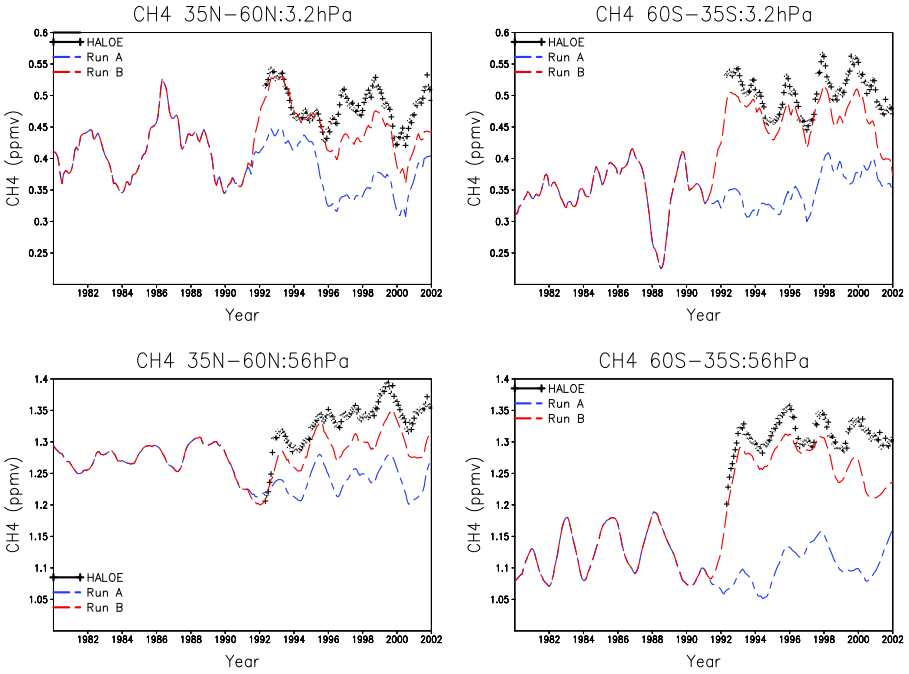

Fig. 4. Variation of CH_4 mixing ratio (ppmv) from 1980–2002 for model runs A (blue dashed) and B (red dashed) for 35° N60° N at 3.2 hPa (~40 km), 35° S60° S at 3.2 hPa, 35° N 60° N at 56 hPa (~20 km), and 35° S60° S at 56 hPa. The model lines have been smoothed with a 12-month running mean. Run C is not shown and is essentially identical to run B. Also shown are monthly mean observations from HALOE (+) from 1992 onwards.

ACPD
12, 12023–12050, 2012

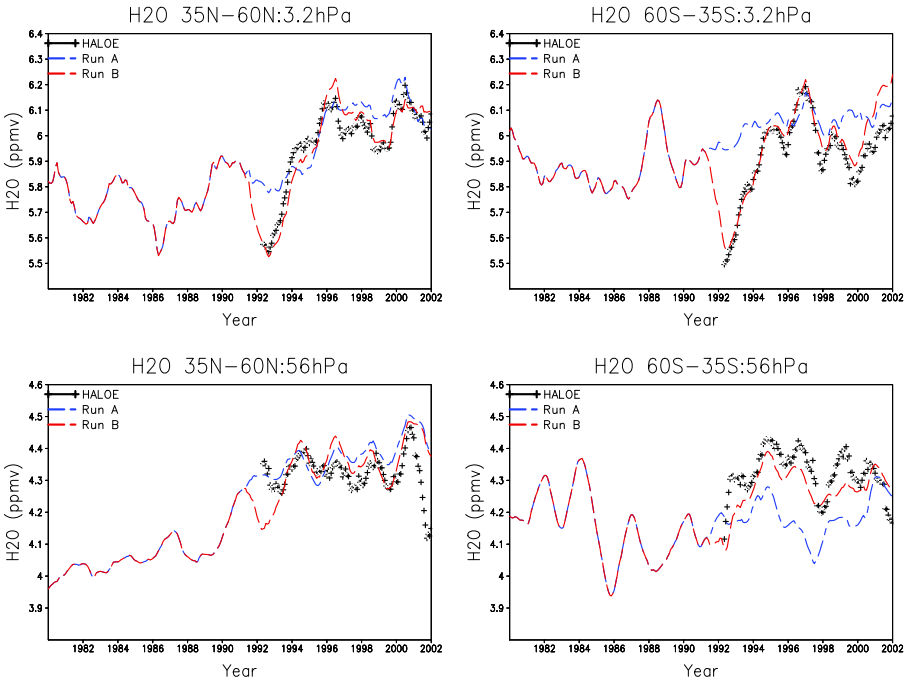

Fig. 5. As Fig. 4 but for H_2O (ppmv). HALOE data is plotted from 1992 onwards.

ACPD
12, 12023–12050, 2012

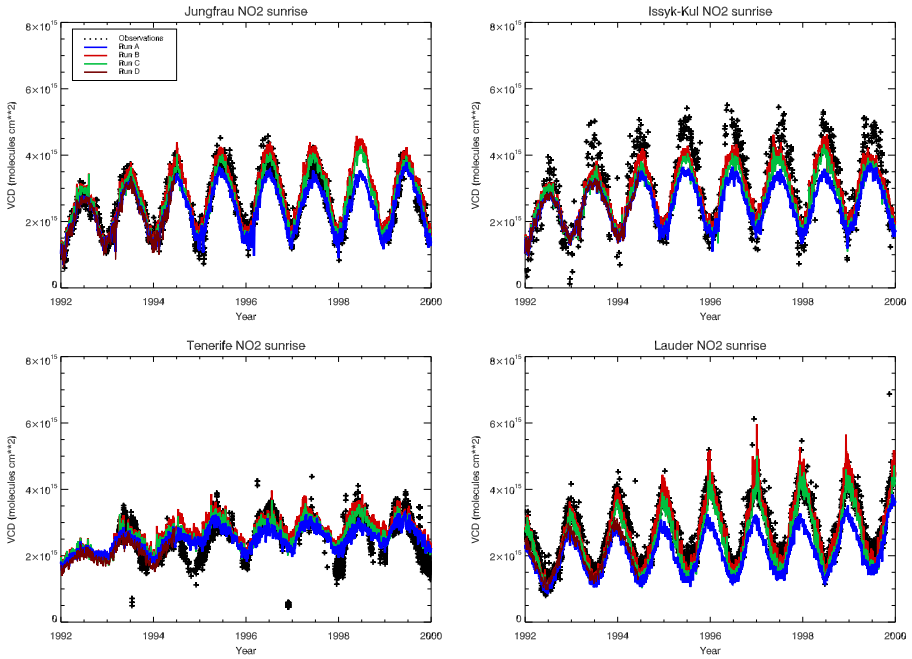

Fig. 6. Observed sunrise vertical columns of NO_2 (molecules cm^{-2}) from 1992 to 2000 at Jungfraujoch (46.3° N, 7.6° E), Issyk-Kul (42.6° N, 77.0° E), Tenerife (28.0° N, 343.0° E), and Lauder (45.0° N, 169.7° E), along with results from model runs A (blue line), B (red line), C (green line) and D (purple line), until end 1992.

ACPD
12, 12023–12050, 2012

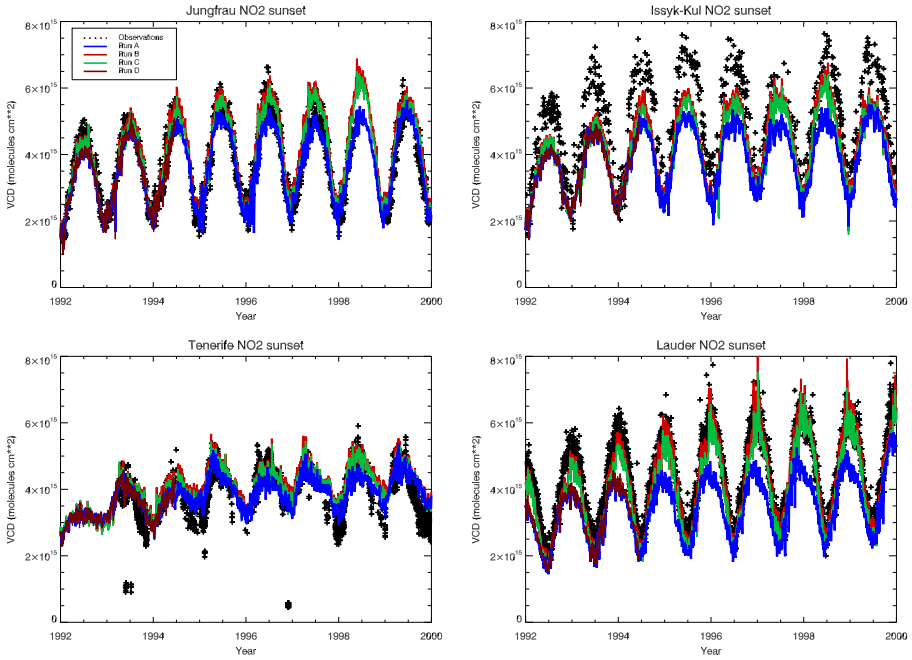

Fig. 7. As Fig. 6 but for sunset column NO_2.

ACPD
12, 12023–12050, 2012

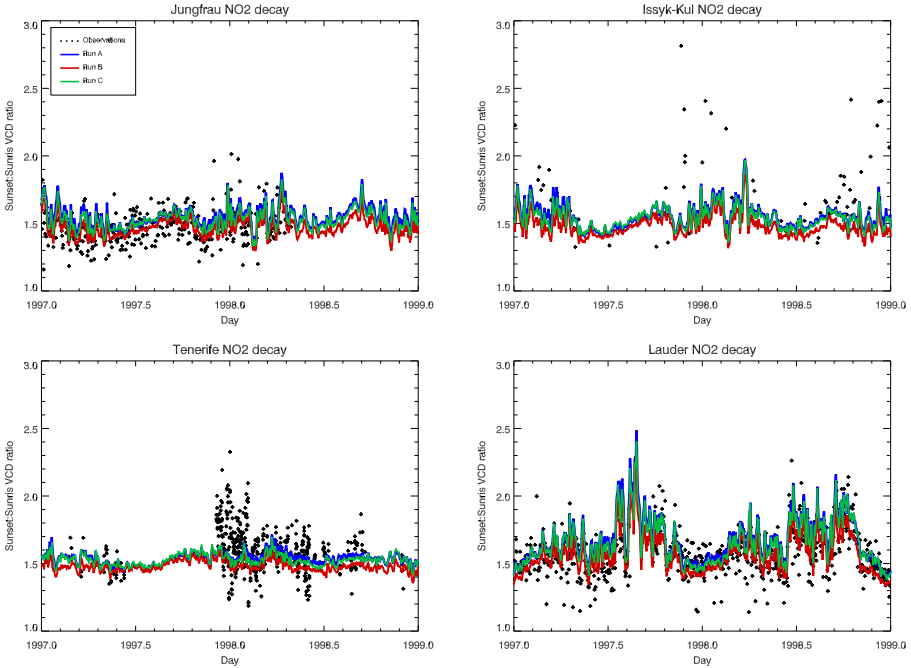

Fig. 8. Ratio of sunset:sunrise NO_2 vertical columns for observations (+) and 3 runs for 1997–1998 for Jungfraujoch, Issyk-Kul, Tenerife and Lauder.

ACPD
12, 12023–12050, 2012