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A linear CO chemistry parameterization in a chemistry-transport model: evaluation and application to data assimilation

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Abstract. This paper presents an evaluation of a new linear parameterization valid for the troposphere and the stratosphere, based on a first order approximation of the carbon monoxide (CO) continuity equation. This linear scheme (hereinafter noted LINCO) has been implemented in the 3D Chemical Transport Model (CTM) MOCAGE. First, a one and a half years of LINCO simulation has been compared to output obtained from a detailed chemical scheme output. The mean differences between both schemes are about 25 ppbv (part per billion by volume) or 15% in the troposphere and 10 ppbv or 100% in the stratosphere. Second, LINCO has been compared to diverse observations from satellite instruments covering the troposphere (Measurements Of Pollution In The Troposphere: MOPITT) and the stratosphere (Microwave Limb Sounder: MLS) and also from aircraft (Measurements of ozone and water vapour by Airbus in-service aircraft: MOZAIC programme) mostly flying in the upper troposphere and lower stratosphere (UTLS). In the troposphere, the LINCO seasonal variations as well as the vertical and horizontal distributions are quite close to MOPITT CO observations. However, a bias of $\sim$ -40 ppbv is observed at 700 hPa between LINCO and MOPITT. In the stratosphere, MLS and LINCO present similar large-scale patterns, except over the poles where the CO concentration is underestimated by the model. In the UTLS, LINCO presents small biases less than 2% compared to independent MOZAIC profiles. Thirdly, we assimilated MOPITT CO using a variational 3D-FGAT (First Guess at Appropriate Time) method in conjunction with MOCAGE for a long run of one and a half years. The data assimilation greatly improves the vertical CO distribution in the troposphere from 700 to 350 hPa compared to independent MOZAIC profiles. At 146 hPa,

the assimilated CO distribution is also improved compared to MLS observations by reducing the bias up to a factor of 2 in the tropics. This study confirms that the linear scheme is able to simulate reasonably well the CO distribution in the troposphere and in the lower stratosphere. Therefore, the low computing cost of the linear scheme opens new perspectives to make free runs and CO data assimilation runs at high resolution and over periods of several years.

1 Introduction

Carbon monoxide (CO) plays an important role in tropospheric chemistry and is one of the main pollutants in the atmosphere. It has also an important impact on the chemical production of tropospheric ozone (O_3) and thereby on climate change (e.g., Stevenson et al., 2006). Its main sink is the reaction with the hydroxyl radical (OH) (Thompson, 1992). The biomass burning of natural vegetation is a significant global source of CO especially with hot spots in Central and South Africa, in South America and in northern Australia, along with photochemical production. Its lifetime of 1-2 months in the troposphere , and its important source emissions (industries, transport, biomass burning) make CO a good tracer of pollution which is indicative of incomplete combustion. It also enables the tracking of long-distance airmass transport (Stohl et al., 2002; Staudt et al., 2001). Various studies have been carried out to characterize transport over polluted continents such as South America (e.g., Pickering et al., 1996; Freitas et al., 2005), Asia (e.g., Li et al., 2005) or Africa (e.g., Sinha et al., 2004; Guan et al., 2008).

Chemistry Transport Models (CTMs) at global scale are used for a better understanding of global atmospheric chemistry since they provide 4–D fields of chemical species. Several tens of species and hundreds of reactions are required to adequately model the chemical production and loss rates of the major active species. For example, O_3 encounters different regimes in the troposphere and in the stratosphere. In the troposphere, O_3 production consists of oxidation reactions between OH and some trace gas constituents in the presence of nitrogen oxide; whereas in the stratosphere, it is produced by a cycle initiated by photolysis of oxygen and destroyed by reactions involving nitrogen oxides, chlorine and bromine species.

Such complete schemes require a large amount of computing time which can put limitations on the model resolutions or on the duration of the feasible simulations. That is why linear ozone parameterizations have been developed for upper tropospheric and stratospheric studies, where only major ingredients of the atmospheric chemistry are taken into account (temperature and ozone amount). For example, the scheme developed by Cariolle and Déqué (1986) computes the ozone chemistry trend around a long state equilibrum defined by O_3 and temperature. This parameterization has been recently updated by Cariolle and Teyssèdre (2007) and is widely used in many models, such as the ARPEGE–Climat general circulation model (Déqué et al., 1994), and the European Centre for Medium-Range Weather Forecasting (ECMWF) model (Andersson et al., 2003) for operational

forecasts and the ERA40 reanalysis project (Oikonomou and O 'Neill, 2006). Several linear ozone parameterizations (e.g., McLinden et al., 2000; McCormack et al., 2004, 2006) were validated by Geer et al. (2007) using data assimilation in a stratosphere-troposphere model. Even if the computing capabilities have increased, linear parameterizations are useful. These parameterizations may avoid the impact of mis-specified or poorly-known chemical species. By construction, such schemes have no intrinsic trend and then are useful for simulations of several years (e.g., Hadjinicolaou et al., 2005) and data assimilation (e.g., Semane et al., 2007; Massart et al., 2009).

In addition to their representation of chemical processes, CTMs may present deficiencies due to approximations in dynamic processes and in emission inventory. Chemical data assimilation can be used to overcome these deficiencies. It consists of providing consistent chemical species 4-D fields by combining in an optimal way observations and model fields (e.g., Lahoz et al., 2007; El Amraoui et al., 2004; Semane et al., 2009). These fields are well suited for the study of transport processes and budget analyses in the troposphere (Pradier et al., 2006), in the stratosphere (El Amraoui et al., 2008b) or in the Upper Troposphere-Lower Stratosphere (UTLS) (Barret et al., 2008). Because chemical linear schemes produce minimal computing cost and relative good quality of simulated fields, it is then possible to perform data assimilation over periods of several years.

The purpose of this paper is to present a new linear parameterization of the CO chemical distribution for the troposphere and the stratosphere, which makes possible long model runs and data assimilation. The parameterization is based on a linearization of the CO tendencies around an equilibrium state, which has been derived from a 2-D photochemical model similarly to the approach used for ozone (Cariolle and Déqué, 1986). This parameterization is well suited for CO which has a relative simple chemistry. The CO linear scheme has been implemented into the Météo-France transport chemical model MOCAGE (Peuch et al., 1999). A free model simulation forced by the ARPEGE meteorological analyses has been performed. A comparison of the model CO outputs with various observational datasets is done for a one and half year period from December 2003 to July 2005. In the stratosphere, the model results are compared to the space-borne Microwave Limb Souder (MLS) observations. In the troposphere, comparisons are made using the space-borne MOPITT (Measurements Of Pollution In The Troposphere) observations and the *in situ* measurements from MOZAIC (Measurements of ozone and water vapour by Airbus in-service aircraft) programme. We also compare the performances of the linear scheme to a detailed chemical scheme, RACMOBUS (Dufour et al., 2004). Besides, the CO linear scheme is used within the MOCAGE-PALM assimilation system (Massart et al., 2005) in order to assimilate the MOPITT CO data during the same period of study (from December 2003 to July 2005). Detailed comparisons of the CO analyses with independent MOZAIC and MLS CO observations are reported in order to validate the experiment.

This paper is organized as follows. In section 2, we describe the CO linear parameterization, the CTM model, the data assimilation system employed as well as the different datasets used in this study. In section 3, we discuss the results obtained for the validation of the free run with the linear

CO chemical scheme. Section 4 presents and validates the analyses of one year of MOPITT CO data assimilation. Lastly, summary and conclusions are presented in section 5.

2 Model and data descriptions

2.1 The linear carbon monoxide chemical scheme

The new linear scheme for the computation of the CO chemical tendencies relies on a methodology similar to the approach developed by Cariolle and Déqué (1986) and updated by Cariolle and Teyssèdre (2007) for stratospheric ozone. The CO continuity equation is expanded into a Taylor series up to the first order around the local value of the CO mixing ratio r_{CO} and the temperature T:

$$\partial r_{CO}/\partial t = A_1 + A_2(r_{CO} - A_3) + A_4(T - A_5) \quad (1)$$

where the A_i terms are monthly averages calculated using the 2D photochemical model MOBIDIC (MOdèle BIDImensionnel de Chimie)(Cariolle et al., 2008):

$A_1 = \overline{(P - L)}$: production minus loss rate of CO

$A_2 = \overline{\partial(P - L)/\partial r_{CO}}$: zonal net variation of (*P-L*) due to r_{CO} variations

$A_3 = \overline{r_{CO}}$: CO zonal mixing ratio

$A_4 = \overline{\partial(P - L)/\partial T}$: zonal net variation of (*P-L*) due to *T* variations

$A_5 = \overline{T}$: zonal mean temperature

with *P* and *L* being the CO production and loss terms, respectively.

The partial derivatives A_2 and A_4 in Eq. (1) are obtained by perturbing the 2D model fields by $\pm 10\%$ for the CO mixing ratio and by ± 10 K for temperature, respectively. For each month, a set of zonal mean coefficients is obtained. To test the accuracy of the linearity of the system, we have applied perturbations (up to $\pm 30\%$ for CO and ± 20 K for temperature), and have found very small deviations in the calculated A_i.

Figure 1a shows the A_3 term for the month of January. It represents the zonal mean distribution of CO from the MOBIDIC model. This CO distribution is characterized by larger mixing ratios within the range of 100-130 ppbv (part per billion by volume) in the troposphere of Northern Hemisphere (NH) and in the lower tropical troposphere. Large vertical gradients are observed near the UTLS region with mixing ratios below 30 ppbv in the lower stratosphere. This CO distribution is comparable to current measurements (e.g., Edwards et al., 2003).

The A_1 term in Figure 1b gives the chemical tendencies needed to balance those due to transport and surface emissions of CO. As expected, this term is negative and large at the equator in the lower troposphere in the presence of large biomass burning and anthropogenic emissions, and rapid vertical transport by the rising branch of the mean meridional circulation and by convection.

The photochemical relaxation time of CO, is given by $\tau = -1/A_2$ (Figure 1c). Since the CO lifetime is mainly controlled by its reaction with OH, the distribution of τ is closely linked to the

OH concentrations. The lowest values of τ, less than 30 days, are found in the equatorial lower troposphere, and in the middle stratosphere outside of the polar vortex (90 S–60 N). From the surface up to the tropopause, the CO relaxation time increases to reach a relative maximum of about 100 days at the equator. At summertime in southern latitudes (90 S–50 S) τ increases to values up to one year in the UTLS. At high latitudes in the NH from 0 to 30 km, τ tends to infinity and CO becomes an inert tracer. Note that for implementation within global models, the CO parameterization is complemented with surface emissions and deposition in a similar way to what is done when a detailed chemical scheme is used (see section 2.2).

2.2 MOCAGE-PALM

MOCAGE (MOdèle de Chimie Atmospherique à Grande Echelle) is a three-dimensional chemistry transport model for the troposphere and stratosphere (Peuch et al., 1999) which simulates interactions between dynamical, physical and chemical processes. MOCAGE uses hybrid vertical levels from the surface up to 5 hPa with a resolution of about 150 m in the lower troposphere (40 m near the surface) and up to 800 m in the lower stratosphere. Hybrid vertical levels are designed so that lowermost levels follow the terrain while upper levels are isobaric. The version of MOCAGE used in this study has an horizontal resolution of 2 °x 2 ° over the globe and uses a semi-Lagrangian advection scheme (e.g., Josse et al., 2004) to transport the chemical species. Turbulent diffusion is calculated with the scheme of Louis (1979) and convective processes with the scheme of Bechtold et al. (2001). The meteorological analyses of Météo-France, ARPEGE (Courtier et al., 1991) were used to force the dynamics of the model every 6 hours.

The linear scheme is compared to the detailed scheme of MOCAGE, RACMOBUS which is a combination of the stratospheric scheme REPROBUS (Lefèvre et al., 1994) and of the tropospheric scheme RACM (Stockwell et al., 1997). It includes 119 individual species with 89 prognostic variables and 372 chemical reactions. The simulations presented here use the emissions inventory from Dentener et al. (2005). For CO, emissions are given as a monthly mean for biomass burning and a yearly mean for others. Emission rates and deposition velocities are computed externally (Michou and Peuch, 2002) and taken into account in MOCAGE. The dry deposition scheme is based upon Wesley (1989) scheme. The wet deposition is parameterized for stratiform and convective clouds (Giorgi and Chameides, 1986; Mari et al., 2000) and validated in (Michou et al., 2004). MOCAGE is used for several applications: operational chemical weather forecasting in Météo-France (Dufour et al., 2004) and data assimilation research (e.g., El Amraoui et al., 2008b; Semane et al., 2009). A detailed validation of the model has been done using a large number of measurements during the Intercontinental Transport of Ozone and Precursors (ICARTT/ITOP) campaign (Bousserez et al., 2007). Its climate version has also been validated over several years by Teyssèdre et al. (2007).

In addition, we used the assimilation system MOCAGE-PALM (Massart et al., 2005). The assimilation module is PALM (Buis et al., 2006) within which is implemented the 3D-FGAT (First

Guess at Appropriate Time) assimilation technique (Fisher and Andersson, 2001). This technique is a compromise between the 3D-Var and the 4D-Var. It has been validated during the assimilation of ENVISAT data project and has producted good quality results compared to independent data and many other assimilation systems (Geer et al., 2006). Details on the method and on the assimilation system can be found in Massart et al. (2005), Massart et al. (2007) and El Amraoui et al. (2010).

2.3 The Measurements

2.3.1 MOPITT

The MOPITT (Measurements Of Pollution In The Troposphere) instrument is a nadir infrared correlation radiometer onboard the NASA Terra Satellite (Drummond and Mand, 1996). It has been monitoring CO from March 2000 to date. It provides global coverage in about 3 days. The pixel size is 22 km x 22 km and the vertical profiles are retrieved on 7 pressure levels (surface, 850, 700, 500, 350, 250 and 150 hPa). The maximum *a posteriori* algorithm (Deeter et al., 2003) is used to retrieve CO from MOPITT measured radiances. It is a statistical combination of the measurement and the *a priori* information based on an optimal estimation method (Rodgers, 2000). The retrieved profiles are characterized by their averaging kernel matrix, which indicates the sensivity of the MOPITT measurements to the true CO profile. In this study, we select MOPITT CO (Version 3) retrieved profiles with less than 40% *a priori* contamination to ensure good quality of dataset validation (Emmons et al., 2009). The accuracy of MOPITT CO retrieved profiles is assumed to be less than 20 ppbv for all of the 7 levels according to Emmons et al. (2004).

2.3.2 MLS

The Microwave Limb Sounder (MLS) (Waters et al., 2006) on Aura spacecraft was launched on July 15th, 2004 and placed into a near-polar Earth orbit at $\sim$705 km with an inclination of 98° and an ascending mode at 13:45 hours. It orbits the Earth around 14 times per day and provides dense spatial coverage for a limb sounder with daily 3500 profiles, between 82°N and 82°S. MLS observes thermal microwave emission from Earth's limb in five spectral regions from 118 GHz to 2.5 THz. The MLS CO measurements are made in the 240 GHz region. The optimal estimation method is used to retrieve CO profiles (Rodgers, 2000). The retrieval grid has 6 levels per pressure decade for altitudes below 0.1 hPa and 3 levels per pressure decade above this. The MLS CO level 2 products used in this paper are produced by version 2.2 of the data processing algorithms. The vertical resolution of MLS CO retrieved profiles is about 3–4 km in the stratosphere and the horizontal resolution is between 500 km for lower stratospheric levels and 300 km for upper stratospheric levels. Data are selected according to quality flag criteria presented in Livesey et al. (2007). In the version used in this study, the impact of extra terrestrial signal generated by the Milky Way and affecting the terrestrial CO retrieval mainly at 22 hPa for some specific days of year and latitudes has been eliminated

according to Pumphrey et al. (2009). The MLS CO data set was validated by Livesey et al. (2008) for the upper troposphere and lower stratosphere and by Pumphrey et al. (2007) for the stratosphere and the mesosphere where the accuracy was estimated to be 30 ppbv for pressure of 147 hPa and less.

2.3.3 MOZAIC

The MOZAIC (Measurements of ozone and water vapour by Airbus in-service aircraft) programme (Marenco et al., 1998) was launched in January 1993. The project results from the collaboration of the aeronautics industry, airline carriers, and research laboratories. Measurements started in August 1994, with the installation of ozone and water vapor sensors aboard five commercial aircrafts. In 2001, the instrumentation was upgraded by installing CO sensors on all aircrafts. For the measurement of CO, the IR gas filter correlation technique is employed (Thermo Environmental Instruments, Model 48CTL). This IR instrument provides excellent stability, which is important for continuous operation without frequent maintenance. The sensitivity of the instrument was improved by several modifications (Nédélec et al., 2003), achieving a precision of 5 ppbv or 5% for a 30 s response time. The majority of these flights are in the NH and connect Europe, North America and eastern Asia, but also include flights to South America and Africa. About 90% of the MOZAIC measurements are made at cruise altitude, between 9 and 12 km. The remaining measurements are performed during ascent and descent phases. A complete description of the MOZAIC programme may be found at http://mozaic.aero.obs-mip.fr/web/ and in the IGAC Newsletters (Cammas and Volz-Thomas, 2007). We selected MOZAIC data from flights over Europe, North America and Eastern Asia.

3 Evaluation of the linear CO chemical scheme

In order to evaluate the linear CO chemical scheme, two MOCAGE simulations have been made in the period between December 1st, 2003 and July 1st, 2005. The first one (hereinafter referred to as LINCO) used the linear CO parameterization and the second one used the detailed chemical scheme RACMOBUS. All the other model components are kept the same: in particular, they both used the same atmospheric forcing from ARPEGE analysis and the same emission inventory. The simulated field for December 1st, 2003 has been obtained from a free run with RACMOBUS started from the October climatological initial field. Independent observations are used to evaluate LINCO: measurements from MOPITT in the troposphere, MLS in the stratosphere and MOZAIC in the UTLS.

3.1 Comparison with the detailed chemical scheme RACMOBUS

In this section, we evaluate the effect of CO chemistry representation in the model (detailed or linearized), by comparing two simulations. Both RACMOBUS and LINCO use the same model

components (e.g., transport, atmospheric processes and emissions). In Figure 2, we present the temporal evolution of the CO zonal mean obtained from LINCO and RACMOBUS for the period from December 2003 to June 2005 at the pressure levels 850 and 150 hPa, in the lowermost and uppermost troposphere respectively. Qualitatively, the two schemes behave similarly with differences between schemes of about ± 20 %, never exceeding ± 40 %. However, at the beginning of the period, LINCO concentrations tend to be higher than RACMOBUS CO concentrations whereas elsewhere, the opposite behavior is observed at both pressure levels: RACMOBUS CO concentrations are higher. The differences between both schemes are lower in the NH than in Southern Hemisphere (SH). Note that both schemes have two different approaches. On the one hand, RACMOBUS is a detailed chemical scheme for which CO is interdependent with other species, particularly the hydroxyl radical (OH). On the other hand, the CO concentration from LINCO is controlled by fixed zonal coefficients based on 2D model outputs (see section 2.1).

Figure 3 presents CO zonal means obtained from LINCO and RACMOBUS for two specific months (July 2004 and January 2005) representative of NH summer and winter, respectively. Both chemical schemes have similar patterns with small differences. The distribution of CO from both schemes reproduces the impact of African biomass burning emissions in the tropics. In the same way, the two schemes capture the mesospheric subsidence of CO within the stratospheric polar vortex (latitudes poleward of 60°) evidenced by high CO concentrations between 25 and 30 km. For both months, concentrations in LINCO are lower than those in RACMOBUS in the troposphere but the differences do not exceed $\sim$25 ppbv ($\sim$35%). The maxima of the difference between both schemes in the troposphere, are located in the region with the intense convective activity, namely the inter-tropical convergence zone.

The negative bias observed in the troposphere between RACMOBUS and LINCO may come from 3 causes. The first hypothesis could be a negative bias between RACMOBUS average values and the A3 coefficient which would lead LINCO to relax towards too low CO concentrations. Figure 1.a and Figure 3 show that the opposite is actually observed: the A_3 coefficient is larger than RACMOBUS and, on the contrary, A_3 tends to increase the concentrations in LINCO. The second hypothesis is a bias between the A_5 LINCO coefficient and the ARPEGE temperature analyses used in MOCAGE. The comparison of these two terms shows that the differences are of the order of 1K and the A4 coefficient values are small in the troposphere, leading to a small contribution of the temperature term A_4(T-A_5). The third explanation could be in one hand an inconsistency between the production minus loss rate (A_1 coefficient) and the transport, in other hand to the different way for representing the emissions in MOBIDIC and MOCAGE. This could introduce a too strong destruction of CO in LINCO scheme. To confirm this hypothesis, we made a sensivitive test (not shown) by increasing the A_1 coefficient of LINCO. This test shows that by changing arbitrarily the A_1 coefficient, the bias between LINCO and RACMOBUS can be reduced in the troposphere. However, the A_1 LINCO coefficient is not anymore consistent with the chemistry and physics of the other coefficients calculated

with MOBIDIC. Therefore, we decided to keep the set of coefficients calculated with MOBIDIC in the next sections.

On the contrary in the stratosphere, LINCO concentrations are higher than RACMOBUS except between 70°S and 90°S in July 2004 and between 60°N and 90°N in January 2005. In these regions, LINCO underestimates the CO concentration of the mesospheric descent compared to RACMOBUS. The absolute difference in the stratosphere is about ∼15ppbv (∼200%). Note that CO concentrations are generally very low in RACMOBUS in the stratosphere compared to LINCO, which explains such high relative differences between both schemes in the stratosphere. The positive bias observed between RACMOBUS and LINCO may be explained by the positive bias between the A_3 LINCO coefficient (Figure 1.a) and RACMOBUS (Figures 3) in the stratosphere which relax LINCO concentrations to higher values. Moreover, the production minus loss rate in the stratosphere (Figure 1.b, A_1 coefficient) is positive which may also contribute to the positive bias between RACMOBUS and LINCO.

In the following sections, we evaluate the LINCO fields in comparison to independent data from satellites and *in situ* measurements.

3.2 Comparison with satellite data in the troposphere

Figure 4 shows the time evolution of CO from December 2003 to June 2005 as obtained by LINCO, RACMOBUS and MOPITT measurements at 700 and 250 hPa in the NH and SH. Note that modeled CO fields have been smoothed by MOPITT averaging kernels in order to take into account the vertical resolution and the *a priori* information used in the retrieval process of the V3 MOPITT product. At 700 hPa (Figure 4c and 4d), the seasonal CO variations are fairly well represented by both chemical schemes showing a maximum in April in the NH and a maximum in October in the SH. April maximum in the NH is due to the very weak sunshine during winter and correspondingly less destruction of CO by OH leading to the buildup of CO because of its long lifetime. In addition, in the SH, this period corresponds to an intense biomass burning activity in South Africa and later on in Australia (Edwards et al., 2006). However, the LINCO scheme presents lower concentrations than RACMOBUS and MOPITT in both hemispheres. As already explained in the previous section, this suggests a larger destruction of CO in LINCO compared to RACMOBUS and MOPITT retrievals. The bias between MOPITT and LINCO is about 30-40 ppbv in the NH and 20-30 ppbv in the SH. However, LINCO follows very well the variations seen in MOPITT CO retrievals with a constant bias. RACMOBUS scheme seems to have a better CO time evolution in the SH than in the NH where emissions patterns and variability as well as photochemistry are more complex. Even if the bias between RACMOBUS and MOPITT is very low in the SH and at 250 hPa in the NH, a negative bias between RACMOBUS and MOPITT is observed in the NH at 700 hPa which can reach 30 ppbv. The bias between measured and modeled CO fields also suggests that CO emissions used in the model are underestimated.

This latter point is highlighted by Figures 5 and 6 which present a comparison, for the specific months of October 2004 and April 2005, between results from LINCO and MOPITT CO retrievals at 700 and 250 hPa, respectively. MOPITT CO at 700 hPa (Figure 5) shows generally high concentrations linked to intense emissions in the NH but also in regions of SH mostly affected by biomass burning such as South America, South Africa or Australia in October 2004. LINCO also underestimates the CO retrieved from MOPITT measurements in April 2005 reinforcing the idea of too much destruction of CO in the linear scheme combined with too low emissions used in CTMs as suggested by Shindell et al. (2006) or lately by Pison et al. (2009).

Nevertheless, LINCO tends to accumulate CO over the Tibetan plateau especially in October 2004 (Figure 5), which is located near populated regions with high emissions. Li et al. (2005) suggested that the boundary layer pollution, transported by Asian summer monsoon convection, is trapped by the Tibetan anticyclone. The model appears to overestimate this accumulation compared to MOPITT data. A same behaviour is observed over the Tibetan plateau using RACMOBUS which confirms that this overestimation is not linked to the LINCO chemistry but rather to transport and dynamics (common to the two simulation). In Figure 6, similar remarks as in Figure 5 can be made, but a smaller bias is noticed between LINCO and MOPITT CO concentrations, $\sim$-20% instead of $\sim$-40% at 750 hPa.

3.3 Comparison with satellite data in the stratosphere

In this section, we compare the LINCO simulation with MLS CO data, in order to evaluate the CO linear scheme in the lower stratosphere. CO fields from LINCO simulation are smoothed by a theoretical triangular averaging kernel with the full-width at half-maximum equal to the MLS vertical resolution according to Pumphrey et al. (2007). This is made to represent the contribution of the range of layers of the atmosphere for which the satellite retrieval is sensitive. This contribution is important in the lower stratosphere where CO vertical gradients are strong. Figure 7 presents the CO monthly zonal means for the month of October 2004 and March 2005 calculated for LINCO and MLS CO. The MLS pressure levels are selected from 146 to 14 hPa. For both months, the vertical and latitudinal gradients of CO in the UTLS for pressures larger than 70 hPa are well represented by the model compared to MLS CO with the same range of mixing ratios except over the poles, where the LINCO mixing ratios are underestimated compared to the CO observed by MLS. This may be explained by a too rapid transport of the meridional circulation observed in ARPEGE analysis used in this study. This behaviour has already been reported by (e.g., van Noije et al., 2004; Monge-Sanz et al., 2006) for ECMWF reanalyses. In the same way, Teyssèdre et al. (2007) present similar behaviour with MOCAGE (using other years of ARPEGE analyses) and show that the age of the air is too young which suggest also a too rapid meridional transport. The mid–stratospheric air, where CO is less concentrated, is transported downward into the lower stratosphere too fast. It leads to smaller CO concentrations than the ones actually found by MLS in the lower stratosphere.

Above the altitude pressure of 20 hPa, an increase of CO is observed by MLS both for the South pole in October 2004 and for the North pole in March 2005. Jin et al. (2009) presents the mesospheric descent observed by MLS, ACE–FTS (Atmospheric Chemistry Experiment Fourier Transform Spectrometer onboard SCISAT–1 satellite), Odin/SMR (Sub-Millimeter Radiometer onboard Odin satellite) and simulated by the Canadian Middle Atmosphere Model at higher altitudes for the same period. Compared to this study, the maximum of CO shown here above 20 hPa only corresponds to the bottom part of the mesospheric descent. The values are underestimated by MOCAGE probably because of the model top, namely located at 5 hPa and constrained by a zonal climatology. Consequently, MOCAGE leads to a mis-representation of the mesospheric descent.

A positive bias is observed between MLS CO and LINCO for pressure levels between 45 and 10 hPa for both months. As explained in section 3.1, the bias may come from the LINCO coefficients (A_1 and A_3) which tend to increase LINCO concentrations at these stratospheric pressure levels.

3.4 Comparison with MOZAIC aircraft data in the UTLS

To evaluate the linear scheme in the UTLS region, we compared CO from MOZAIC aircraft data and model output interpolated on-line at flight times and locations. We averaged the observations where pressures are lower than 300 hPa into boxes of 2°x 2° in order to match the model resolution. In Figure 8, the LINCO and the MOZAIC data are compared for the months of October 2004 and April 2005 which correspond to CO maxima in the SH and in the NH, respectively. In both cases, LINCO tends to overestimate the aircraft observations, with very low biases, less than 2%, but with a large standard deviation of ∼27%. This indicates that LINCO does not present a systematic bias at the levels between 300 hPa and 180 hPa. However, as expected, LINCO is not able to represent the variability observed by aircraft *in situ* measurements. In October 2004, the model represents well the spatial distribution of CO as observed by MOZAIC. Both observations and model show a meridional gradient between equator and high latitudes as aircraft fly in the lower stratosphere at mid-latitudes (low CO amounts of ∼50 ppbv) and in the troposphere at low latitudes (high CO amounts of ∼80 ppbv). An overestimation of the LINCO concentration is observed over the Tibetan Plateau, where the model accumulates CO as described in section 3.2. In April 2005, an increase of CO is observed by MOZAIC over polluted areas in the South-Center USA and over Asia. The model underestimates this increase of CO concentration in the higher troposphere as was concluded in section 3.2 by comparison with MOPITT CO.

4 Evaluation of a one year of MOPITT CO data assimilation with the linear scheme

4.1 Assimilation diagnostics

The linear scheme of CO is used here to demonstrate its great interest for data assimilation over long periods of time due to its low computational cost. The assimilation experiment started on

December 1st, 2003 and ended on July 1st, 2005. The initial 3D field of atmospheric constituents is the same as for twin runs for LINCO and RACMOBUS discussed in section 3. MOPITT data are averaged in boxes of 2° x 2 ° to obtain super-observations directly assimilated into the used version of MOCAGE-PALM system. Moreover, in order to take into account of the vertical resolution of the MOPITT measurements, their averaging kernels as well as their a priori profiles are considered in the assimilation procedure. Note that the variance-covariance error matrices of MOPITT measurements are also taken into account during the assimilation process through the error covariance matrix of the observations. The analysed fields are studied for the period between July 2004 and July 2005. The period prior to July, 1st 2004 is assumed to be perturbed by spinup effects, and thus is not considered in our analysis.

We check the consistency of the observations minus analyses (OMA) and observations minus forecast (OMF) in order to evaluate the quality of the CO assimilated fields. Figure 9 shows the two distributions of OMA and OMF for all of the 7 MOPITT levels and for the full period (July 2004-July 2005). Both distributions are nearly Gaussian and therefore are assumed to have a Gaussian error. The mean of OMF values is close to zero ($\sim$0.7 ppbv) with a standard deviation of $\sim$16.6 ppbv, which indicates a small bias between MOPITT observations and model forecast. The standard deviation and the mean value of OMA (with a correlation coefficient of 0.99) are smaller than that of OMF (with a correlation coefficient of 0.94) which shows that the analyses are closer to the observations than the forecast. This again indicates that the assimilation system behaves properly.

4.2 Evaluation of CO analyses

4.2.1 Comparison in the troposphere with independent MOZAIC aircraft data

In this section, we use MOZAIC CO as independent data in order to evaluate MOPITT CO assimilated fields (hereinafter referred to MOPan) and the LINCO simulation (reference standard simulation) with the objective to determine the added-value of data assimilation. Table 1 presents correlation, bias and standard deviations between LINCO and MOZAIC CO, and between MOPan and MOZAIC CO. LINCO underestimates CO in the lower troposphere with a negative bias of -25% compared to MOZAIC at 700 hPa whereas MOPan reduces this bias to a positive value of 8.6%. These results are consistent with the bias of +5% obtained by Emmons et al. (2009) directly considering MOPITT and MOZAIC in 2004 over coincident profiles. In this study, we consider all MOZAIC profiles and not only MOPITT coincident profiles as done by Emmons et al. (2009) which may lead to a slightly different bias (+8% instead of +5%). As presented in section 3.4, the model tends to increase the CO concentrations in the UTLS region. This may explain the differences between a $\sim$16% bias found between MOZAIC data and MOPan at 250 hPa and a $\sim$2% bias between MOZAIC and MOPITT CO data found by Emmons et al. (2009) for the same period.

In order to go a step further in our analysis, CO averaged profiles are presented over 3 regions of

the globe: North America (140–30 W, 15–70 N), Europe (20 W–40 E, 15–75N) and Asia (60–160 E, 5–50 N) and for the different seasons: NH summer, autumn, winter and spring 2004–2005. In Figure 10, MOZAIC CO profiles are plotted on 8 isobars at 950, 850, 750, 650, 550, 450, 350 and 250 hPa, averaged within the 8 layers: surface–900 hPa, 900–800 hPa, 800–700 hPa, 700–600 hPa, 600–500 hPa, 500–400 hPa, 400–300 hPa and 300–220 hPa respectively. For all cases, except over Asia during NH summer, LINCO underestimates CO concentration compared to MOZAIC CO with a negative bias of ∼40 ppbv at 850 hPa, decreasing with altitude until 250 hPa where the negative bias is very low (∼10 ppbv). The assimilation of MOPITT CO data improves greatly the vertical distribution of CO which shows MOPan profiles closer to the MOZAIC independent data than free run LINCO for pressures between 750 to 350 hPa. However, compared to MOZAIC, MOPan overestimates CO at 850 hPa in October-November-December 2004 and January-February-March 2005 over Europe and North America. Nevertheless, 850 hPa is probably not the most MOPITT reliable level for MOPITT data according to Emmons et al. (2004). In the lower troposphere and over Asia, LINCO slightly overestimates CO in summer (July-August-September) but widely underestimates CO during the other seasons. This is probably due to a mis-specified fossil fuel burning in the inventory emissions of the model over Asia as suggested by Shindell et al. (2006). The data assimilation corrects this discrepancy by decreasing CO concentration in summer and increasing CO elsewhere. Moreover, the annual added CO mass in the troposphere by the MOPITT CO assimilation (via the assimilation increment) is estimated to 680 Tg. This corresponds to ∼68% of the total mass introduced during one year by the emission inventory.

4.2.2 Comparison in the UTLS with MLS

MOZAIC data are only available up to 190 hPa, therefore we used independent MLS data at 147 hPa which is nearly an overlapped level with MOPITT at 150 hPa to evaluate MOPan at higher altitude. We applied the same theorical triangular averaging kernel as described in section 3.3. In Figure 11, we compare MLS CO to LINCO and MOPan simulated CO interpolated at MLS locations at 146 hPa. For October 2004, the results calculated with LINCO are different from the corresponding MLS CO fields. Over South America, CO fields from LINCO are quite similar to MLS observations. Conversely, over Africa, there is an underestimation of CO concentration compared to MLS data probably inducing the stronger underestimation over South East Asia due to horizontal and vertical transport deficiencies and also to too much CO destruction and too low emissions over Africa in the linear scheme. In the same way, for April 2005, the same behavior is observed as for October 2004, with strong underestimation of CO mainly over Africa. For both months, MOPITT CO data assimilation corrects these underestimates by increasing CO concentration over Africa and South East Asia. MOPan improves the quality of the CO distribution compared to MLS into the tropics by reducing the bias between the model and the observations from -15% without assimilation to 5% and increasing the correlation from 0.65 without assimilation to 0.75 with assimilation. At

extratropical latitudes the bias between MLS and MOPan is higher (-50%) because MOPITT data are more scattered and therefore the low model values due to the too rapid meridional circulation (as described in section 3.3) are predominant. Moreover the MLS data are assumed to have an uncertainty of ± 30 % according to Livesey et al. (2008), which may also contribute to this high difference between MOPITT CO analyses and MLS CO at high latitudes.

5 Summary and Conclusions

In this study, we have presented a new linear parameterization for CO (LINCO) which can be used both in the troposphere and in the stratosphere. In order to evaluate this linear chemical scheme, we have implemented the parameterization into the MOCAGE CTM. In a first part, the results of LINCO have been compared to the detailed chemical scheme of MOCAGE, RACMOBUS. LINCO results have also been compared to several CO measurements from satellite instruments (MOPITT in the troposphere and MLS in the stratosphere) and from *in situ* aircraft data (MOZAIC) in the UTLS. In a second part, we have assimilated MOPITT CO with LINCO over one and a half years and compared analyses to independent observations (MOZAIC and MLS) to evaluate the quality of the results. This evaluation was done to demonstrate the interest of the LINCO low computation cost which allows data assimilation over long periods of time.

The CO distributions of both the linear and the detailed chemical schemes behave qualitatively similarly. The linear scheme has smaller CO concentrations in the troposphere and larger CO concentrations in the stratosphere compared to RACMOBUS. We deduced that these differences are mainly due in the troposphere to a too high destruction of CO concentration by the production minus loss rate LINCO coefficient (A_1). In the stratosphere the positive bias between LINCO and RACMOBUS, is partly due to the positive bias between the CO climatological coefficient (A_3) and RACMOBUS. However differences between the two chemical schemes remain quite small (less than 30 ppbv). The comparisons between model results and MOPITT CO data globally show a good agreement. The model is able to capture the main spatial patterns of CO and to represent the seasonal CO variations with a maximum in the NH in April and a maximum in the SH in October as observed in MOPITT data. A negative bias of LINCO in the troposphere is observed, predominant in the NH with a maximum near the surface (30-40 ppbv at 850 hPa) and a decrease with altitude (20 ppbv at 250 hPa). In the lower and middle stratosphere, LINCO simulates very well the CO concentrations distributions except at the poles where CO concentrations are underestimated. We suggest that this deficiency in LINCO is related to a too rapid downward transport of poor CO air from middle stratosphere to the lower stratosphere at the poles. In the UTLS, we obtained a very good agreement between LINCO results and MOZAIC CO observations with a small bias of +2% but with a large variability of $\pm 27\%$.

The MOPITT CO analyses generally show a good agreement with the MOZAIC observations

and reduce the negative bias in the troposphere compared to the model without assimilation and MOZAIC (from ∼-20% without assimilation to ∼+8% with assimilation). At 250 hPa, the bias between MOPITT CO analyses and MOZAIC is larger than the bias between MOPITT CO and MOZAIC CO obtained by Emmons et al. (2009) probably because of the model transport deficiency. We compared MOZAIC CO profiles with LINCO profiles over North America, Europe and Asia for different seasons. In each case, the assimilation greatly improves the CO vertical distribution from 700 to 350 hPa. The annual added CO mass in the troposphere by the MOPITT CO assimilation is estimated to 680 Tg, which corresponds to ∼68% of the total mass introduced by the emission inventory during one year. MOPITT CO analyses also present a good agreement with MLS data at 146 hPa. However, at extratropical latitudes, MOPITT CO analyses underestimate CO concentration compared to MLS CO (∼-50%). This bias may be related to a too rapid downward transport of the meridional circulation.

Finally, we show that the linear parameterization for CO, introduced in a CTM, is able to represent reasonably well the main CO distribution in the troposphere and the lower stratosphere. The main advantage of such chemical scheme is its low computing cost (only one tracer) which makes possible simulation and data assimilation for long periods. It is now possible to assimilate data at higher global resolution (for example 0.5° instead of 2° actually used) to use the full horizontal resolution of current nadir satellite–borne instruments.

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References

Andersson, E., Beljaars, A., Bidlot, J., Miller, M., Simmons, A., and Thepaut, J. N.: A major new cycle of the IFS: cycle 25R4, in: ECMWF Newsletter 97, ECMWF, Shinfield Park, Reading,Berkshire RG2, 9AX, UK, 2003.

Barret, B., Ricaud, P., Mari, C., Attié, J.-L., Bousserez, N., Josse, B., Flochmoën, E. L., Livesey, N. J., Massart, S., Peuch, V.-H., Piacentini, A., Sauvage, B., Thouret, V., and Cammas, J.-P.: Transport pathways of CO in the African upper troposphere during the monsoon season: a study based upon the assimilation of spaceborn observations, Atmos. Chem. Phys., 8, 3231–3246, 2008.

Bechtold, P., Bazile, E., Guichard, F., Mascart, P., and Richard, E.: A mass-flux convection scheme for regional and global models, Quart. J. Roy. Meteor. Soc., 127, 869–886, 2001.

Bousserez, N., Attié, J.-L., Peuch, V.-H., Michou, M., Pfister, G., Edwards, D., Emmons, L., Mari, C., Barret, B., Arnold, S. R., Heckel, A., Richter, A., Schlager, H., Lewis, A., Avery, M., Sachse, G., Browell, E. V., and Hair, J. W.: Evaluation of the MOCAGE chemistry transport model during the ICARTT/ITOP experiment, J. Geophys. Res., 112, doi:10.1029/2006JD007595, 2007.

Buis, S., Piacentini, A., and Déclat, D.: PALM: a computational framework for assembling high-performance computing applications, Concurrency Computat.: Pract. Exper., 18, 231–245, 2006.

Cammas, J.-P. and Volz-Thomas, A.: The MOZAIC program (1994–2007), International Global Atmospheric Chemistry (IGAC) Newsletter, Issue N.37, November 2007, 2007.

Cariolle, D. and Déqué, M.: Southern hemisphere medium-scale waves and total ozone disturbances in a spectral general circulation model, J. Geophys. Res., 91, 10 825–10 846, 1986.

Cariolle, D. and Teyssèdre, H.: A revised linear ozone photochemistry parameterization for use in transport and general circulation models: multi-annual simulations, Atmos. Chem. Phys., 7, 2183–2196, 2007.

Cariolle, D., Evans, M., Chipperfield, M., Butkovskaya, N., Kukui, A., and Lebras, G.: Impact of the new HNO_3-forming channel of the HO_2+NO reaction on tropospheric HNO_3, NO_x, HO_x and ozone, Atmos. Chem. Phys., 8, 4061–4068, 2008.

Cathala, M. L., Pailleux, J., and Peuch, V.-H.: Improving chemical simulations of the upper troposphere–lower stratosphere with sequential assimilation of MOZAIC data, Tellus, 55B, 1–10, 2003.

Clark, H. L., Cathala, M.-L., Teyssèssdre, H., Cammas, J.-P., and Peuch, V.-H.: Cross-tropopause fluxes of ozone unsing assimilation of MOZAIC observations in a global CTM, Tellus, 59B, 39–49, 2007.

Courtier, P., Freydier, C., Geleyn, J., Rabier, F., and Rochas, M.: The ARPEGE project at Météo France, in: Atmospheric Models, vol.2, pp. 193–231, Workshop on Numerical Methods, Reading, U.K., 1991.

Deeter, M., Emmons, L., Francis, G., Edwards, D., Gille, J., Warner, J., Khattatov, B., Ziskin, D., Lamarque, J., SP, S. H., Yudin, V., Attié, J.-L., Packman, D., Chen, J., Mao, D., and Drummond, J.: Operational carbon monoxide retrieval algorithm and selected results for the MOPITT instrument, J. Geophys. Res., 108, doi: 10.1029/2002JD003186, 2003.

Dentener, F., Stevenson, D., Cofala, J., Mechler, R., Amann, M., Bergamaschi, P., Raes, F., and Derwent, R.: The impact of air pollutant and methane emission controls on tropospheric ozone and radiative forcing: CTM calculations for the period 1990–2030, Atmos. Chem. Phys., 5, 1731–1755, 2005.

Déqué, M., Dreveton, C., Braun, A., and Cariolle, D.: The ARPEGE/IFS atmosphere model: a contribution to the French community climate modelling, Clim. Dynam., 10, 249–266, 1994.

Drummond, J. R. and Mand, G. S.: Evaluation of operational radiances for the Measurement of Pollution in the Troposphere (MOPITT) instrument CO thermal-band channels, J. Geophys. Res., 109, doi:10.1029/2003JD003970, 1996.

Dufour, A., Amodei, M., Ancellet, G., and Peuch, V.-H.: Observed and modelled ”chemical weather” during ESCOMPTE, Atmos. Res., 74, 161–189, 2004.

Edwards, D. P., Lamarque, J.-F., Attié, J.-L., Emmons, L. K., Richter, A., Cammas, J.-P., Gille, J. C., Francis, G. L., Deeter, M. N., Warner, J., Ziskin, D. C., Lyjak, L. V., Drummond, J. R., and Burrows, J. P.: Tropospheric ozone over the tropical Atlantic: A satellite perspective, J. Geophys. Res., 108, doi:10.1029/2002JD002927, 2003.

Edwards, D. P., Petron, G., Novelli, P. C., Emmons, L. K., Gille, J. C., and Drummond, J. R.: Southern Hemisphere carbon monoxide interannual variability observed by Terra/Measurement of Pollution in the Troposphere (MOPITT), J. Geophys. Res., 111, doi:10.1029/2006JD007079, 2006.

El Amraoui, L., Ricaud, P., Urban, J., Théodore, B., Hauchecorne, A., Lautié, N., de La Noë J, J., Guirlet, M., Flochmën, E. L., Murtagh, D., Dupuy, E., Frisk, U., and dÁndon, O.: Assimilation of Odin/SMR O_3 and N_2O measurements in a three-dimensional chemistry transport model, Quart. J. Roy. Meteor. Soc., 109, doi:10.1029/2004JD004796, 2004.

El Amraoui, L., Peuch, V.-H., Ricaud, P., Massart, S., Semane, N., Teyssèdre, H., Cariolle, D., and Karcher, F.: Ozone loss in the 2002–2003 Arctic vortex deduced from the assimilation of Odin/SMR O3 and N2O measurements: N2O as a dynamical tracer, Quart. J. Roy. Meteor. Soc., 134, 217–228, 2008a.

El Amraoui, L., Semane, N., Peuch, V.-H., and Santee, L.: Investigation of dynamical processes in the polar stratospheric vortex during the unusually cold winter 2004/2005, Geophys. Res. Lett., 35, doi:10.1029/2007GL031251, 2008b.

El Amraoui, L., Attié, J.-L., Semane, N., Claeyman, M., Peuch, V.-H., Warner, J., Ricaud, P., Cammas, J.-P., Piacentini, A., Cariolle, D., Massart, S., and Bencherif, H.: Midlatitude stratosphere–troposphere exchange as diagnosed by MLS O3 and MOPITT CO assimilated fields, Atmos. Chem. Phys., 10, 2175–2194, 2010.

Emmons, L., Deeter, M., Gille, J., Edwards, D., Attié, J.-L., Warner, J., Ziskin, D., Francis, G., Khattatov, B., Lamarque, V. Y. J.-F., Ho, S., Mao, D., Chen, J., Drummond, J., Novelli, P., Sachse, G., Coffey, M., Hannigan, J., Gerbig, C., Kawakami, S., Kondo, Y., Takegawa, N., Schlager, H., Baehr, J., and Ziereis, H.: Validation of Measurements of Pollution in the Troposphere (MOPITT) CO retrievals with aircraft in situ profiles, J. Geophys. Res., 109, doi:10.1029/2003JD004101, 2004.

Emmons, L., Edwards, D., Deeter, M., Gille, J., Campos, T., Nédélec, P., Novelli, P., and Sachse, G.: Measurements of Pollution In The Troposphere (MOPITT) validation through 2006, Atmos. Chem. Phys., 9, 1795–1803, 2009.

Fisher, M. and Andersson, E.: Developments in 4D-Var and Kalman filtering, in: Technical Memorandum Research Department, vol. 347, ECMWF, Reading, UK, 2001.

Freitas, S., Longo, K., Dias, M. S., Dias, P. S., Chatfield, R., Prins, E., Axtaxo, P., and Recuero, F.: Monitoring the transport of bimoass burning emissions in South America, Environ. Fluid. Mech., 5, 135–167, doi:10.1007/s1065200502437, 2005.

Giorgi, F. and Chameides, W.: Rainout lifetimes of highly soluble aerosols and gases as inferred from simulations with a general circulation model, J. Geophys. Res., 91(D13), 14 367–14 376, 1986.

Geer, A., Lahoz, W., Jackson, D., Cariolle, D., and McCormack, J.: Evaluation of linear ozone photochemistry parametrizations in a stratosphere-troposphere data assimilation system, Atmos. Chem. Phys., 7, 939–959, 2007.

Geer, A. J., Lahoz, W. A., Bekki, S., Bormann, N., Errera, Q., Eskes, H. J., Fonteyn, D., Jackson, D. R., Juckes, M. N., Massart, S., Peuch, V.-H., Rharmili, S., and Segers, A.: The ASSET intercomparison of ozone analyses: Method and first results, Atmos. Chem. Phys., 6, 5445–5474, 2006.

Guan, H., Chatfield, R., Freitas, S., Bergstrom, R., and Longo, K.: Modeling the effetc of plume-rise on the transport of carbon monoxide over Africa with NCAR CAM, Atmos. Chem. Phys., 8, 6801–6812, 2008.

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

Jin, J. J., Semeniuk, K., Beagley, S. R., Fomichev, V. I., Jonsson, A. I., McConnell, J. C., Urban, J., Murtagh, D., Manney, G. L., Boone, C. D., Bernath, P. F., Walker, K. A., Barret, B., Ricaud, P., and Dupuy, E.: Comparison of CMAM simulations of carbon monoxide (CO), nitrous oxide (N2O), and methane (CH4) with observations from Odin/SMR, ACE-FTS, and Aura/MLS, Atmos. Chem. Phys., 9, 3233–3252, 2009.

Josse, B., Simon, P., and Peuch, V.-H.: Radon global simulationwith the multiscale chemistry trasnport model MOCAGE, Tellus, 56, 339–356, 2004.

Lahoz, W. A., Errera, Q., Swinbank, R., and Fonteyn, D.: Data assimilation of stratospheric constituents: a review, Atmos. Chem. Phys., 7, 5745–5773, 2007.

Lefèvre, F., Brasseur, G., Folkins, I., Smith, A., and Simon, P.: Chemistry of the 1991–1992 stratospheric winter: three dimensional model simulations, J. Geophys. Res., 99, 8183–8195, 1994.

Li, Q., Jiang, J., Wu, D., Read, W., Livesey, N., Waters, J., Zhang, Y., Wang, B., Filipiak, M., Davis, C., Turquety, S., Wu, S., Park, R., Yantosca, R. M., and Jacob, D.: Convective outflow of South Asian pollution: A global CTM simulation compared with EOS MLS observations, Geophys. Res. Lett., 32, doi:10.1029/2005GL022762, 2005.

Livesey, N., Read, W., Lambert, A., Cofield, R., Cuddy, D., Froidevaux, L., Fuller, R., Jarnot, R., Jiang, J., Jiang, Y., Knosp, B., Kovalenko, L., Pickett, H., Pumphrey, H., Santee, M., Schwartz, M., Stek, P., Wagner, P., Waters, J., and Wu, D.: EOS MLS version 2.2 Level 2 data quality and description document, *Tech. Rep.* JPL D-33509, Jet Propul. Lab., Pasadena, Calif., 2007.

Livesey, N., Filipiak, M., Froidevaux, L., Read, W., Lamber, A., Santee, M., Jiang, J., Pumphrey, H., Waters, J., Cofield, R., Cuddy, D., ad B.J. Drouin, W. D., Fuller, R., Jarnot, R., Jiang, Y., Ksnop, B., Li, Q., Perun, V., Schwartz, M., Snyder, W., Stek, P., Thurstans, R., Wagner, P., M.Avery, Browell, E., Cammas, J.-P., Christensen, L., G.S.Diskin, Gao, R.-S., Jost, H.-J., Loewenstein, M., Lopez, J., P.Nedelec, Osterman, G., G.W.Sachse, and Webster, C.: Validation of Aura Microwave Limb Sounder O_3 and CO observations in the upper troposphere and lower stratosphere, J. Geophys. Res., 113, doi:10, 2008.

Louis, J.-F.: Parametric model of vertical eddy fluxes in the atmosphere, Boundary Layer Meteorol., 17, 187–202, 1979.

Mari, C., Jacob, D. J., and Bechtold, P.: Transport and scavenging of soluble gases in a deep convective cloud, J. Geophys. Res., 105(D17), 22 255–22 267, 2000.

Marenco, A., Thouret, V., Nédélec, P., Smit, H., Helten, M., Kley, D., Karcher, F., Simon, P., Law, K., Pyle, J.,

Poschmann, G., von Wrede, R., Hume, C., and Cook, T.: Measurement of ozone and water vapour by Airbus in-service aircraft: the MOZAIC airborne program, An overview, J. Geophys. Res., 103, 25 631–25 642, 1998.

Massart, S., Cariolle, D., and Peuch, V.-H.: Towards an improvement of the atmospheric ozone distribution and variability by assimilation of satellite data, C. R. Geosci., 337, 1305–1310, 2005.

Massart, S., Piacentini, A., Cariolle, D., El Amraoui, L., and Semane, N.: Assessment of the quality of the ozone measurements from the Odin/SMR instrument using data assimilation, Can. J. Phys., 85, 1209–1223, 2007.

Massart, S., Clerbaux, C., Cariolle, D., Piacentini, A., Turquety, S., and Hadji-Lazaro, J.: First steps towards the assimilation of IASI ozone data into the MOCAGE-PALM system, Atmos. Chem. Phys., 9, 5073–5091, 2009.

McCormack, J., Eckermann, S., Coy, L., Allen, D., Kim, Y.-J., Hogan, T., Lawrence, B., Stephens, A., Broweel, E., Burris, J., McGee, T., and Trepte, C.: NOGAPS-ALPHA model simulations of stratospheric ozone during the SOLVE2 campaign, Atmos. Chem. Phys., 4, 2401–2423, 2004.

McCormack, J. P., Eckermann, S. D., Siskind, D. E., and Coy, L.: A new linearized gas-phase ozone photochemistry parameterization for high-altitude NWP and climate models, Atmos. Chem. Phys., 6, 4943–4972, 2006.

McLinden, C., Olsen, S., Hannegan, B., WIld, O., Prather, M., and Sundet, J.: Stratospheric ozone in 3-D models: A simple chemistry and the corss-tropopause flux, J. Geophys. Res., 105, 14 653–14 665, 2000.

Michou, M. and Peuch, V.-H.: Surface exchanges in the MOCAGE multiscale Chemistry and Transport Model, Water Res., 15, 173–203, 2002.

Michou, M., Laville, P., Serca, D., Fotiadi, A., Bouchou, P., and Peuch, V.-H.: Measured and modeled dry deposition velocities over the ESCOMPTE area, Atmos. Res., 47, 89–116, 2004.

Monge-Sanz, B. M., Chipperfield, M. P., Simmons, A. J., and Uppala, S. M.: Mean age of air and transport in a CTM: Comparison of different ECMWF analyses, Geophys. Res. Lett., 34,L04801, doi: 10.1029/2006GL028515, 2006.

Nédélec, P., Cammas, J.-P., Thouret, V., G., G. A., Cousin, J.-M., Legrand, C., Abonnel, C., Lecoeur, F., Cayez, G., and Marizy, C.: An improved infra-red carbon monoxide analyser for routine measurements aboard commercial Airbus aircraft: Technical validation and first scientific results of the MOZAIC III Program, Atmos. Chem. Phys., 3, 1551–1564, 2003.

Oikonomou, E. K. and O 'Neill, A.: Evaluation of ozone and water vapor fields from the ECMWF reanalysis ERA40 during 1991–1999 in comparison with UARS satellite and MOZAIC aircraft observations, J. Geophys. Res., 111, doi:10.1029/2004JD005341, 2006.

Peuch, V.-H., Amodei, M., Barthet, T., Cathala, M. L., Michou, M., and Simon, P.: MOCAGE, MOdéle de Chimie Atmosphérique à Grande Echelle, in: Proceedings of Météo France: Workshop on atmospheric modelling, pp. 33–36, Toulouse, FRANCE, 1999.

Pickering, K., Thompson, A., Y., W., Tao, W., Namara, D., Kirchhof, J., Sachse, G., Bradshaw, J., Gregory, G., and Blaki, D.: Convective transport of biomass burning emissions over Brazil during TRACEA, J. Geophys. Res., 101, 23 993–24 012, 1996.

Pison, I., Bousquet, P., Chevallier, F., Szopa, S., and Hauglustaine, D.: Multi-species inversion of CH_4, CO and

H_2 emissions from surface measurements, Atmos. Chem. Phys., 9, 5281–5297, 2009.

Pradier, S., Attié, J.-L., Chong, M., Escobar, J., Peuch, V.-H., Lamarque, J.-F., Khattatov, B., and Edwards, D.: Evaluation of 2001 springtime CO transport over West Africa using MOPITT CO measurements assimilated in a global chemistry transport model, Tellus, 58B, 163–176, 2006.

Pumphrey, H., Filipiak, M., Livesey, N., Schwartz, M., Boone, C., Walker, K., Bernath, P., Ricaud, P., Barret, B., Clerbaux, C., Jarnot, R., Manney, G., and Waters, J.: Validation of middle–atmosphere carbon monoxide retrievals from the Microwave Limb Sounder on Aura, J. Geophys. Res., 112, doi:10.1029/2007JD008723, 2007.

Pumphrey, H. C., Cofield, R. E., Filipiak, M. J., and Livesey, N. J.: An all-sky survey at 230 GHz by MLS on Aura, Adv. Space Res., 43(3), 342–348, 2009.

Ricaud, P., Attié, J.-L., Teyssèdre, H., El Amraoui, L., Peuch, V.-H., Matricardi, M., and Schluessel, P.: Equatorial total column of nitrous oxide as measured by IASI on MetOp-A: implications for transport processes, Atmos. Chem. Phys., 9, 3947–3956, 2009.

Rodgers, C.: Inverse Methods for Atmospheric Sounding: Theory and Practice, vol. 2 of *Series on Atmospheric, Oceanic and Planetary Physics*, World Scientific, 2000.

Semane, N., Peuch, V.-H., Amraoui, L. E., Bencherif, H., Massart, S., Cariolle, D., Attié, J.-L., and Abidab, R.: An observed and analysed stratospheric ozone intrusion over the high Canadian Arctic UTLS region during the summer of 2003, Quart. J. Roy. Meteor. Soc., 133, 171–178, 2007.

Semane, N., Peuch, V.-H., Pradier, S., Desroziers, G., El Amraoui, L., Brousseau, P., Massart, S., Chapnik, B., and Peuch, A.: On the extraction of wind information from the assimilation of ozone profiles in MtoFrance 4D-Var operational NWP suite, Atmos. Chem. Phys., 9, 4855–4867, 2009.

Shindell, D., Faluvegi, G., Stevenson, D., Krol, M., Emmons, L., Lamarque, J.-F., Petron, G., Dentener, F., Ellingsen, K., Schultz, M., Wild, O., Amann, M., Atherton, C., Bergmann, D., Bey, I., Butler, T., Cofala, J., Collins, W., Derwent, R., Doherty, R., Drevet, J., Eskes, H., Fiore, A., Gauss, M., Hauglustaine, D., Horowitz, L., Isaksen, I., Lawrence, M., Montanaro, V., Muller, J.-F., Pitari, G., Prather, M., Pyle, J., Rast, S., Rodriguez, J., Sanderson, M., Savage, N., Strahan, S., Sudo, K., Szopa, S., Unger, N., van Noije, T., and Zeng, G.: Multimodel simulations of carbon monoxide: Comparison with observations and projected near–future changes, J. Geophys. Res., 111, doi:10.1029/2006JD007100, 2006.

Sinha, P., Jaegle, L., Hobbs, P., and Liang, Q.: Transport of biomass burning emissions from Southern Africa, J. Geophys. Res., 106, doi:10.1029/2004JD005044, 2004.

Staudt, A., Jacob, D., Logan, J., Bachiochi, D., Krishnamurti, T., and Sachse, G.: Continental sources, transoceanic transport, and interhemispheric exchange of carbon monoxide over the Pacific, J. Geophys. Res., 106, 32 571–32 590, 2001.

Stevenson, D. S., Dentener, F. J., Schultz, M. G., Ellingsen, K., van Noije, T. P. C., Wild, O., Zeng, G., Amann, M., Atherton, C. S., Bell, N., Bergmann, D. J., Bey, I., Butler, T., Cofala, J., Collins, W. J., Derwent, R. G., Doherty, R. M., Drevet, J., Eskes, H. J., Fiore, A. M., Gauss, M., Hauglustaine, D. A., Horowitz, L. W., Isaksen, I. S. A., Krol, M. C., Lamarque, J.-F., Lawrence, M. G., Montanaro, V., ller, J.-F. M., Pitari, G., Prather, M. J., Pyle, J. A., Rast, S., Rodriguez, J. M., Sanderson, M. G., Savage, N. H., Shindell, D. T., Strahan, S. E., Sudo, K., and Szopa, S.: Multimodel ensemble simulations of present-day and near-future tropospheric ozone, J. Geophys. Res., 111, doi:10.1029/2005JD006338, 2006.

Stockwell, W., Kirchner, F., M. Khun, M., and Seefeld, S.: A new mechanism for regional atmospheric chemistry modelling, J. Geophys. Res., 102, 25 847–25 879, 1997.

Stohl, A., Eckhardt, S., Forster, C., James, P., and Spichtinger, N.: On the pathways and timescales of intercontinental air pollution transport, J. Geophys. Res., 107, 4684, doi:10.1026/2001JD001396, 2002.

Teyssèdre, H., Michou, M., Clark, H. L., Josse, B., Karcher, F., Olivié, D., Peuch, V.-H., Saint-Martin, D., Cariolle, D., Attié, J.-L., Nédélec, P., Ricaud, P., Thouret, V., van der A, R. J., Volz-Thomas, A., , and Chéroux, F.: A new tropospheric and stratospheric Chemistry and Transport Model MOCAGE-Climat for multi-year studies: evaluation of the present-day climatology and sensitivity to surface processes, Atmos. Chem. Phys., 7, 5815–5860, 2007.

Thompson, A.: The Oxidizing Capacity of the Earths Atmosphere: Probale Past and Future Changes, Science, 256, 1157–1165, 1992.

van Noije, T. P. C., Segers, A. J., and van Velthoven, P. F. J.: Implications of the enhanced Brewer-Dobson circulation in European Centre for Medium-Range Weather Forecasts reanalysis ERA–40 for the stratosphere-troposphere exchange of ozone in global chemistry transport models, J. Geophys. Res., 109, doi:0.1029/2004JD004586, 2004.

Waters, J., Froidevaux, L., Harwood, R., Jarnot, R., Pickett, H., Read, W., Siegel, P., Cofield, R., Filipiak, M., Flower, D., Holden, J., Lau, G., Livesey, N., Manney, G., Pumphrey, H., Santee, M., Wu, D., Cuddy, D., Lay, R., Loo, M., Perun, V., Schwartz, M., Stek, P., Thurstans, R., Boyles, M., Chandra, K., Chavez, M., Chen, G., Chudasama, B., Dodge, R., Fuller, R., Girard, M., Jiang, J., Jiang, Y., Knosp, B., LaBelle, R., Lam, J., Lee, K., Miller, D., Oswald, J., Patel, N., Pukala, D., Quintero, O., Scaff, D., Snyder, W. V., Tope, M., Wagner, P., and Walch, M.: The Earth Observing System Microwave Limb Sounder (EOS MLS) on the Aura satellite, IEEE Trans. Geosci. Remote Sens., 44(5), 1075–7092, 2006.

Wesley, M. J.: Parameterization of surface resistances to gazeous dry deposition in regional-scale numerical models, Atmos.-Environ., 23, 1293–1304, 1989.

Fig. 1. (a) Background CO distribution in parts per billion by volume (ppbv), (b) net photochemical rate (ppbv/days) and (c) photochemical relaxation time (days) as a function of altitude and latitude for the month of January.

Fig. 2. LINCO (left) and RACMOBUS (right) zonal mean of CO in parts per billion by volume(ppbv) from December 2003 to June 2005 at 150 hPa (top) and 850 hPa (middle). Corresponding relative differences (LINCO-RACMOBUS)/RACMOBUS x100 in % are plotted at bottom at 150 (left) and 850 hPa (right).

Fig. 3. Zonal monthly mean of CO from LINCO and RACMOBUS in parts per billion by volume (ppbv) and difference (LINCO-RACMOBUS) (ppbv) on July 2004 (top) and January 2005 (bottom). The isolines correspond to the relative difference of LINCO and RACMOBUS (LINCO-RACMOBUS)/RACMOBUS x100 in %.

	LINCO-MOZAIC		MOPAN-MOZAIC	
Pressure (hPa)	**Corr**	**Bias %**	**Corr**	**Bias %**
250	0.69	-0.1±26.8	0.69	16.2±31.9
350	0.54	-8.8±23.3	0.62	10.8±26.2
500	0.31	-21.0±17.2	0.50	7.2±18.3
700	0.26	-25.5±25.8	0.42	8.6±24.6

Table 1. Mean correlation bias and standard deviation in % between MOZAIC aircraft CO data set and the LINCO run and between the MOPITT CO assimilated fields at 700 (775-600), 500 (600-425) 350 (425-260) and 250 (260-240) hPa.

Fig. 4. CO fields in parts per billion by volume (ppbv) calculated by LINCO (black lines) and by RACMOBUS (red lines) and retrieved from MOPITT measurements (green lines) for NH (a) (left) and SH (b) (right) at 250 hPa (upper panel) and at 700 hPa (c) and (d) (lower panel). Note that modeled CO fields have been smoothed by MOPITT averaging kernels.

Fig. 5. CO fields in parts per billion by volume (ppbv) at 700 hPa calculated by LINCO smoothed by MOPITT averaging kernels (left), MOPITT CO (ppbv) (middle) and corresponding relative differences (%) (Model-Obs)/Obs x100 in October 2004 (upper panels) and April 2005 (lower panels).

Fig. 6. Same as Figure 5 but for 250 hPa.

Fig. 7. Zonal monthly mean of CO from LINCO (left) and MLS (middle) in parts per billion by volume (ppbv) and corresponding relative differences (%) (right) for October 2004 (upper panel) and March 2005 (lower panel). Pressure levels are selected from 146 to 14 hPa. Note that LINCO mixing ratios have been smoothed by triangular MLS averaging kernels.

Fig. 8. CO fields from LINCO (left) and measured by MOZAIC aircraft (center) in parts per billion by volume (ppbv) and corresponding relative differences (%) (right) (Model-Obs)/Obs x100 in October 2004 (upper panel) and April 2005 (lower panel) for pressures between 300 and 180 hPa.

Fig. 9. Histograms of Observations Minus Analyses (OMA: solid lines) and Observations Minus Forecast (OMF:dashed lines) for the 7 MOPITT levels (surface, 850, 700, 500, 350, 250 and 150 hPa) and from July 2004 to July 2005.

Fig. 10. Mean profiles of CO in parts per billion by volume (ppbv) from LINCO (green lines), MOZAIC (black lines) and MOPITT CO assimilated fields (red lines) in 2004-2005 NH summer (JAS) autumn (OND) winter (JFM) and spring (AMJ) over North America (right), Europe (center) and Asia (right).

Fig. 11. CO fields calculated by LINCO (left), assimilated MOPITT CO (center) and MLS CO (right) in parts per billion by volume (ppbv) in October 2004 (upper panel) and April 2005 (lower panel) at 146 hPa. Note that LINCO and assimilated MOPITT CO have been smoothed by triangular MLS averaging kernels.