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balloon profiles**

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Midlatitude ClO during the maximum atmospheric chlorine burden: in situ balloon measurements and model simulations

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Abstract

Chlorine monoxide (ClO) plays a key role in stratospheric ozone loss processes at midlatitudes. We present two balloonborne in situ measurements of ClO conducted in northern hemisphere midlatitudes during the period of the maximum of total inorganic chlorine loading in the atmosphere. Both ClO measurements were conducted on board the TRIPLE balloon payload, launched in November 1996 in León, Spain, and in May 1999 in Aire sur l'Adour, France. For both flights a ClO daylight and night time vertical profile could be derived over an altitude range of approximately 15–31 km. ClO mixing ratios are compared to model simulations performed with the photochemical box model version of the Chemical Lagrangian Model of the Stratosphere (CLaMS). Simulations along 24-h backward trajectories were performed to study the diurnal variation of ClO in the midlatitude lower stratosphere. Model simulations for the flight launched in Aire sur l'Adour 1999 show a good agreement with the ClO measurements. For the flight launched in León 1996, a similar good agreement is found, except at around ≈ 650 K potential temperature (≈ 26 km altitude). However, a tendency is found that for solar zenith angles greater than 86° – 87° the simulated ClO mixing ratios substantially overestimate measured ClO by approximately a factor of 2.5 or more for both flights. Therefore we conclude that no indication can be deduced from the presented ClO measurements that substantial uncertainties exist in midlatitude chlorine chemistry of the stratosphere. An exception is the situation at solar zenith angles greater than 86° – 87° where model simulations substantially overestimate ClO observations.

1. Introduction

Stratospheric ozone has globally decreased over the last ≈ 25 years. In midlatitudes, the vertical, latitudinal, and seasonal characteristics of changes in ozone are broadly consistent with the understanding that halogens are the primary cause of these changes (WMO, 2003). Downward ozone trend of -1 to -3% per decade is estimated

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for the lower stratosphere in the northern and southern hemisphere midlatitudes for the time period between 1979 and 2000 (Wang et al., 2002; WMO, 2003). Furthermore, it was found that the large ozone depletions determined for the Arctic vortex in several previous winters will ultimately spread out and dilute ozone concentrations at midlatitudes and thus contribute to the observed ozone decrease at midlatitudes (e.g. Chipperfield, 1999; Knudsen and Grooß, 2000; Marchand et al., 2004). The catalytic loss of ozone in the lower stratosphere is controlled by a combination of cycles involving reactions with BrO, ClO, HO₂, and NO₂ (e.g. Wennberg et al., 1994; Stimpfle et al., 1994). Thus a prerequisite for a reliable calculation of halogen-induced ozone loss rates at midlatitudes is information about ClO concentrations at midlatitudes and an understanding of the dependence of ClO concentrations on altitude and time of day.

Nonetheless, measurements of ClO at midlatitudes in the lower stratosphere are rare. Early balloonborne in situ measurements of ClO were made in the late 1970's and 1980's all launched in Palestine (32° N), Texas, (e.g. Anderson et al., 1977, 1980; Anderson, 1978). Balloonborne in situ measurements (e.g. Toohey et al., 1993a) and remote measurements (e.g. Osterman et al., 1997) of ClO was obtained at somewhat higher latitudes (launched from Fort Sumner, 34.5° N, New Mexico) in the 1990's. In situ measurements of ClO conducted on board the ER-2 aircraft cover a greater range of the midlatitudes (e.g. Toohey et al., 1991, 1993b; King et al., 1991), but cover only a rather small altitude range of ≈16–20 km. Global or near global measurements of ClO exist from the Microwave Limb Sounder (MLS) aboard the Upper Atmosphere Research Satellite (UARS) (e.g. Ricaud et al., 2000) and the Millimeter-wave Atmospheric Sounder (MAS) during three space shuttle missions in 1992, 1993, and 1994 (e.g. Feist et al., 2000). The analysis of ClO measurements from the recently launched MIPAS-E and ODIN instruments has focussed on the polar regions so far (e.g. Glatthor et al., 2004; Urban et al., 2004). In summary, at midlatitudes (≈ 35° N–60° N), in situ as well as remote measurements of ClO over the entire altitude range of the lower stratosphere (≈15–30 km) are very sparse.

As a result of the Montreal Protocol and its amendments and adjustments, in 1997–

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1998 the total inorganic chlorine stopped increasing in the troposphere and has remained fairly constant since that time, that is the loading of inorganic chlorine Cl_y in the unperturbed stratosphere has recently stabilized (WMO, 2003). Here we present the only two balloonborne in situ measurements of ClO performed in the lower stratosphere at midlatitudes during the period of the maximum of total inorganic chlorine loading in the atmosphere. Both ClO in situ measurements were conducted on board the TRIPLE balloon payload launched in November 1996 in León (42.3° N), Spain, and in May 1999 in Aire sur l'Adour (43.7° N), France. Both flights were optimized in a way that both a vertical ClO daylight and night time profile could be measured over an altitude range of approximately 15–31 km.

Further, photochemical model studies were performed using the box model version of the Chemical Lagrangian Model of the Stratosphere (CLaMS) (McKenna et al., 2002a,b) to test if model simulations can reproduce the diurnal behavior of ClO at midlatitudes over the entire range of the lower stratosphere. In previous photochemical model studies for midlatitude conditions based on ER-2 measurements, the ClO photochemistry was described correctly by models (e.g. Brune et al., 1990; Salawitch et al., 1994; Stimpfle et al., 1994), however discrepancies in the understanding of the chlorine budget remained unresolved at that time (e.g. Stimpfle et al., 1994). In a model study based on balloonborne in situ measurements of ClO (Avallone et al., 1993), observed ClO was greater by as much as a factor of four below 20 km altitude. Studies on the broadband photolysis of ClONO_2 led to the speculation that a pressure dependence of the ClONO_2 quantum yield beyond 300 nm exists (Nickolaissen et al., 1996), but first in situ measurements of ClONO_2 on board the ER-2 aircraft during the northern high-latitude summer found no evidence in support of a pressure-dependent quantum yield for photodissociation of ClONO_2 (Stimpfle et al., 1999). Further, no evidence was found from these ER-2 measurements in support of missing inorganic chlorine species that would constitute a significant fraction of Cl_y (Bonne et al., 2000). In our study, we found in general a quite good agreement between measurements and simulations of the diurnal variation of ClO, but for solar zenith angles (SZA) larger than 86°–87° the

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simulated ClO mixing ratios substantially overestimate measured ClO for both flights.

2. Observations

The ClO measurements were conducted on board the balloonborne multi-instrument payload TRIPLE launched on 14 November 1996 from León (42.3° N, 5.4° W), Spain, and on 3 May 1999 from the French launching base in Aire sur l'Adour (43.7° N, 0.3° W), France (in the following referred to as León and Aire flights). TRIPLE consists of the Jülich ClO/BrO in situ instrument (Vogel et al., 2003), the cryogenic whole air sampler of the University of Frankfurt (Schmidt et al., 1987) for the observation of long-lived tracers and various CFCs from which the amount of total inorganic chlorine, Cl_y, can be inferred (Schmidt et al., 1994; Engel et al., 1997), and the Jülich Fast In Situ Stratospheric Hygrometer (FISH) (Schiller et al., 2002).

On 14 November 1996, a prototype of the Jülich ClO/BrO in situ instrument (Pier-son et al., 1999; Woyke et al., 1999) was flown, whereas on 3 May 1999 the new Jülich ClO/BrO in situ instrument (Vogel et al., 2003) was part of the payload. Both instruments employ the well-established chemical-conversion resonance-fluorescence technique (Brune et al., 1989).

2.1. Meteorological situation

The dynamical situation of the stratosphere was very different for the two balloon flights. The flight in November 1996 was conducted during the typical time period of the formation of the Arctic polar vortex in the northern hemisphere, whereas the flight in May 1999 took place after the dissipation of the polar vortex in spring (see Fig. 1).

The meteorological analysis of FU Berlin for the flight in November 1996 shows that in October 1996, the Arctic polar vortex was stronger developed than normal. In early November the vortex was split and the center of the vortex was displaced out of the pole towards Greenland. From 7 November, the center of the vortex moved

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eastward which caused a temperature decrease and an increase in potential vorticity over Northern Spain until 11 November. Afterwards, the wind speed decreased over Northern Spain, because the center of the vortex moved further on eastward. On 14 November 1996, León was located outside the polar vortex. The air masses probed on this day were previously led around the Atlantic anticyclone and had crossed the cold area over Island in the lower stratosphere.

The flight in May 1999 occurred after a weak northern winter. Through most of the Arctic winter 1998/1999, the polar vortex was abnormally warm and weak, because an atypically early major stratospheric sudden warming occurring in mid-December. A second major warming followed in late February (Manney et al., 1999). As a consequence the vortex was eroded at the time of the flight as obvious from Fig. 1.

2.2. Flight profiles

To study in detail the sunrise evolution of the CIO mixing ratios both flights were launched during sunrise (see Fig. 2). During ascent a CIO night and sunrise profile and during descent a CIO daylight profile could be derived.

On 14 November 1996, the TRIPLE payload was launched at approximately 06:30 UT. After reaching a maximum altitude of approximately 31 km (≈ 10 hPa), a balloon float took place in the 79° – 74° solar zenith angle (SZA) interval. During descent SZAs between 74° and 63° were encountered.

On 3 May 1999, the TRIPLE payload was launched at approximately 03:30 UT. The entire balloon ascent was conducted during night ($\text{SZA} > 87^\circ$). After reaching a maximum altitude of approximately 31 km (≈ 10 hPa), the balloon floated at this altitude between 87° and 80° SZA into sunrise, so that within this air mass the increase of the CIO mixing ratios could be measured. During descent a CIO daylight profile was measured between 80° and 65° SZA.

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2.3. ClO and O₃ measurements

The ClO vertical profiles measured by the TRIPLE balloon payload on 14 November 1996 and on 3 May 1999 are shown in Fig. 3.

On 14 November 1996, a ClO profile was measured during ascent with ClO mixing ratios of up to 150 pptv at float altitude. During descent a ClO daylight profile was measured with ClO peak values of approximately 220 pptv between 750 and 800 K potential temperature. In Fig. 3 (left panel), ozone mixing ratios are shown which were measured simultaneously by an ECC (electrochemical concentration cell) ozone sonde on board TRIPLE. The signal of the ozone sonde was jammed, so that not for all altitudes ozone measurements could be obtained. Therefore in Fig. 3 (left panel) in addition, an ozone profile is shown measured by an ozone sonde launched in León one day after the balloon flight on 15 November 1996. Above 650 K potential temperature, the ozone measurements on 15 November are much lower than on 14 November 1996.

The balloon ascent on 3 May 1999, was during night, so that very low ClO mixing ratios, lower than 50 pptv were measured (see Fig. 3, right panel). On the float level, ClO mixing ratios increase during sunrise up to approximately 130 pptv. For the ClO daylight profile measured during descent, maximum ClO mixing ratios of approximately 200 pptv were obtained at around 840 K potential temperature. Additionally in Fig. 3 (right panel), an ozone profile simultaneously measured by an ECC ozone sonde on board TRIPLE is shown.

For both flights, the overall accuracy of the ClO measurement is $\approx 20\text{--}23\%$. For measured ClO mixing ratios below 50 pptv we deduced an error of ± 10 pptv.

3. Model simulations

Model simulations were performed to investigate whether the measured diurnal variation of chlorine monoxide can be reproduced at midlatitudes over the altitude range between 20 and 31 km. ClO mixing ratios measured at one particular level of poten-

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tial temperature during ascent and descent yield two points within the diurnal variation of ClO. Therefore differences in ClO mixing ratios between ascent and descent can be used to test our understanding of the photochemical evolution of ClO for sunrise, similar as in the model study by Pierson et al. (1999). Here we use for the model simulations the Chemical Lagrangian Model of the Stratosphere (CLaMS) (McKenna et al., 2002a,b). This model simulates both the chemistry of multiple air parcels and their transport and is used here as a photochemical box model. The absorption cross sections and reaction rate constants are taken from standard recommendations (Sander et al., 2002). Usually for simulations with the CLaMS model, the family concept (IMPACT) is employed as the integration solver (McKenna et al., 2002b). In all model simulations presented in this work, the explicit stiff solver SVODE (McKenna et al., 2002b) is used that is both more precise and numerically more expensive. As input data for the photolysis scheme an ozone profile is derived from model results of the Mainz 2-D model (Gidel et al., 1983; Grooß, 1996) below 15 km altitude and from Observations of the Halogen Occultation Experiment (HALOE) on board the UARS satellite (Russell et al., 1993) above 15 km altitude.

We performed simulations along 24-h backward trajectories calculated from the locations of the measurement starting at different levels of potential temperature between 500 K and the float altitude (≈ 865 K–900 K) and for different SZA during float (see Figs. 6 and 7). We calculated these backward trajectories using wind data from the UK Met Office (UKMO) analyses. A chemical initialization has to be determined for the simulations at each level of potential temperature. All available stratospheric measurements, together with tracer-correlations, and model simulations were used as sources for this initialization. In the following, the initialization and the results of the model simulations are described for both balloon flights.

3.1. Simulations for the flight on 3 May 1999

Table 1 gives an overview over the measurements employed in order to derive the initialization of the major important species for the model simulations. We calculate the

temporal development of the chemical trace species along each 24-h backward trajectory perpetually using the results of the previous model simulation to initialize the following 24-h simulation. This is done for all species, except for ozone. To initialize ozone for each cycle the O_3 mixing ratios measured by the ECC ozone sonde on board TRIPLE (case a) (see Sect. 2.3) are used. If ozone would not be reinitialized to measured values, the simulated ozone mixing ratios increase steadily (see below). After approximately 6–9 cycles depending on altitude, the most chemical species converge to a constant volume mixing ratio for a given time in the simulation (see Fig. 4). Additionally, model simulations using different initializations for the partitioning between HNO_3 and N_2O_5 (cf. Table 1) converge to the same ClO mixing ratios after approximately 9 cycles. The volume mixing ratios of the important species used to initialize the model simulations for the last cycle are shown in Table 2.

To study the sensitivity to the initial O_3 mixing ratios, model simulations were performed using the simulated O_3 mixing ratios of the previous model simulation to initialize the following 24-h simulation (case b) as it is done for all other species in the standard simulation (case a). Then, ozone is continuously increasing during the simulation period of 9 times 24 h. Under such conditions, the ozone production rate is larger than the ozone loss during the simulation period of 24 h (see e.g. Fig. 5 lowest panel; the last cycle of case a). For case a, the ozone production rate per day increases with altitude of up to ≈ 300 ppbv at float altitude during the last cycle. A comparison of case a and case b with the ClO measurements shows that the model simulations are sensitive to the initial ozone mixing ratios (see Fig. 6). In contrast to expectation, case b yields a better agreement with the ClO measurements as case a. Nevertheless, ClO simulations for both cases are within the uncertainties of the ClO measurements, whereby for both cases for the night time ClO profile ($SZA > 87^\circ$) the model simulations are at the upper limit of the measurements.

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3.2. Simulations for the flight on 14 November 1996

For the León flight, no measurements of long-lived tracers from the cryogenic whole air sampler on board the TRIPLE payload are available because of technical problems with the sealing of the air samples. Thus no measurement of either CH_4 or N_2O and no information about the total amount of inorganic chlorine Cl_y is available. Therefore to initialize the model simulations we use measurements of the Halogen Occultation Experiment (HALOE) on board the UARS satellite (Russell et al., 1993) and tracer-tracer correlations.

For November 1996, HALOE measurements are available in northern hemisphere midlatitudes within 35°N – 50°N for the time period of 1–5 November and of 15–22 November. Thus for 14 November, the day of the TRIPLE flight, no HALOE observations exist in the in northern hemisphere midlatitudes. Performing a potential vorticity (PV) analysis of the HALOE measurements yields that the HALOE measurements were conducted both within and outside of the polar vortex depending on longitude due to the distinct asymmetric form of the vortex that was shifted away from the North Pole. From meteorological analysis the air masses probed during the TRIPLE flight were led around the polar vortex before the measurement (cf. Sect. 2.1). Therefore we derived two data sets to initialize the model simulations one for midlatitude air masses (case 1) and one for polar air masses (case 2). The following PV criterion was used to separate midlatitude and polar air masses:

Midlatitude			
Θ	600 K	700 K	900 K
PV	<70 PVU	<120 PVU	<400 PVU
Vortex			
Θ	600 K	700 K	800 K
PV	>80 PVU	>150 PVU	>300 PVU

The PV criterion was determined by analyzing the $\text{PV}-\text{CH}_4$ and the O_3-CH_4

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correlations observed by HALOE. Table 1 gives an overview over the sources of the most important species used to initialize the model simulations.

5 Similar as for the Aire flight, we calculate the chemistry along each 24-h backward trajectory perpetually using the results of the previous model simulation to initialize the following 24-h simulation, except for ozone (cf. Sect. 3.1). Above 700 K, ClO mixing ratios resulting from the different simulation cycles converge to a constant value for a given time in the simulation. Below 700 K, no convergence of the ClO mixing ratios was reached within 9 cycles, but the differences between simulated and measured ClO mixing ratios are less than the uncertainties of the ClO measurement. The volume
10 mixing ratios of the major important species used to initialize the model simulations for the last cycle are shown in Table 3 (case 1) and Table 4 (case 2).

Model simulations using different initializations for the partitioning between HNO_3 and N_2O_5 (case 1 and 3 for midlatitude conditions and case 2 and 4 for vortex conditions; cf. Table 1) do not converge after 9 cycles for all altitudes to the same ClO mixing ratios
15 in contrast to the simulations for the Aire flight (see Fig. 7). Only after approximately 30 cycles simulations using different initializations for the partitioning between HNO_3 and N_2O_5 would converge to the same ClO mixing ratios. Thus the simulations are sensitive on the partitioning of the NO_y species in contrast to the simulations of the Aire flight.

20 For midlatitude conditions, simulations reproduce the shape of the measured diurnal variation of ClO, but simulated ClO mixing ratios are slightly below the lower limit of the uncertainties of the ClO measurement during float and daylight, except at 500 K potential temperature (see Fig. 7). For vortex conditions, simulated and measured ClO mixing ratios show a good agreement, except during daylight between 600 and 650 K. Here the maximum of the distribution is shifted to larger SZAs compared to the measurements (see Fig. 7). At 650 K, the ClO daylight profile can not be reproduced
25 by model simulations using either midlatitude or vortex conditions. Here the model simulations underestimate the measurements up to a factor of approximately two. The diurnal variation of ClO and various other species are shown in Fig. 8.

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For the Aire flight the simulated ClO mixing ratios are sensitive to the initial ozone mixing ratios. Therefore model simulations were performed using the simulated O₃ mixing ratios of the previous model simulation to initialize the following 24-h simulation as for the other species (not shown here). The sensitivity of the ClO mixing ratios on initial O₃ mixing ratios determined in this way is negligible in comparison to the sensitivity on the initialization conditions employed in case 1–4.

Ozone is continuously decreasing over the different simulation cycles of up to 9 for both case 1 and 2 up to 700 K potential temperature and is continuously increasing for both cases above 700 K. This shows that the ozone production rate is less than the ozone loss up to 700 K and larger above 700 K during the simulation period of 24 h. Thus for the last cycle an ozone loss of up to approximately –10 ppbv/day below 700 K and an ozone production of up to approximately 50 ppbv/day (case 1) and approximately 80 ppbv/day (case 2) at 900 K potential temperature was found.

3.2.1. Discrepancy for daylight ClO at around 650 K

Possible reasons for the discrepancy between simulations and measurements for the ClO daylight profile at around 650 K will be discussed. At midlatitudes, chlorine nitrate is formed by the reaction of ClO with NO₂ and dissociated in ultraviolet (e.g. Brasseur and Solomon, 1984):



Thus the concentration of daylight ClO depends on the concentration of night time ClONO₂. Therefore underestimated ClO mixing ratios would imply that ClONO₂ is underestimated and thus HCl is overestimated by the model. But simulations initialized with HCl mixing ratios reduced by about 20% (equivalent to approximately the minimum HCl mixing ratios measured by HALOE) still underestimate the ClO measurements after 9 cycles. Further in the lower stratosphere, ClO is inversely correlated with

NO₂ (Stimpfle et al., 1994). To initialize the model simulations, the NO_x mixing ratios are reduced by about 20% (equivalent to approximately the minimum NO_x mixing ratios measured by HALOE), whereby also the initial NO₂ is reduced. Nonetheless the measured ClO mixing ratios are still underestimated by the simulations after 9 cycles.

5 For the Aire flight we found that ClO is sensitive to the initial ozone mixing ratios (cf. Sect. 3.1). For the León flight, we used a mean ozone profile derived from HALOE measurements for midlatitude (case 1) and vortex (case 2) air masses, because the signal of the ozone sonde on board TRIPLE was jammed (cf. Sect. 2.3). At 650 K potential temperature, measurements of the ozone sonde are available and are approximately 0.6 ppmv (for midlatitude conditions) and 1.8 ppmv (for vortex conditions) greater than the corresponding mean ozone mixing ratios derived from HALOE measurements. The simulations at 650 K were repeated using the measurement of the ozone sonde for initialization. After 9 cycles the simulations yield higher ClO mixing ratio for both daylight and night conditions, but still underestimate the ClO daylight measurement and simultaneously overestimate the ClO nighttime measurement (not shown here). In summary it is unlikely that uncertainties in the initialization of HCl, NO_x, and O₃ cause the discrepancies in the ClO daylight profile at around 650 K.

The quantum yields of the two ClONO₂ photolysis channels (ClONO₂ + hν → ClO + NO₂ and ClONO₂ + hν → Cl + NO₃) are taken from standard recommendations (Sander et al., 2002). Nickolaisen et al. (1996) observed pressure dependence of the quantum yield for the ClONO₂ photolysis beyond 300 nm. If model simulations do not consider the effect of pressure on the ClONO₂ photolysis, they would expect that models would tend to over-predict HCl and under-predict ClONO₂ and thus ClO mixing ratios in the lower stratosphere. In our study, to reproduce ClO mixing ratios measured during daylight by model simulations J_{ClONO₂} would have to be increased by a factor of two or more (for case 1 and 2). In this case, the measured ClO nighttime and float profiles would be overestimated substantially by model simulations. Thus it is unlikely that uncertainties in J_{ClONO₂} are the major source of the discrepancies between measurements and simulations in the ClO daylight

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profile. Furthermore, the quantum yield for the ClONO₂ photolysis channels beyond 300 nm was modified in model simulations. Even by neglecting the Cl+NO₃ channel in favor of the ClO+NO₂ channel beyond 300 nm, no evidence is found here that a significant change in the quantum yield has any influence on ClO mixing ratios.

5 [Avallone et al. \(1993\)](#) found in a comparison of ClO in situ balloon measurements and model simulations a good agreement, except below 20 km altitude, where observed ClO is greater by as much as a factor of four. A mechanism responsible for maintaining these high ClO mixing ratios was at that time unclear, whereas reaction rates and absorption cross-sections are taken from [DeMore et al. \(1992\)](#). In our study,
10 we found no discrepancies below 20 km altitude between measured and simulated ClO mixing ratios using reaction rate constants and absorption cross-sections from current standard recommendations ([Sander et al., 2002](#)). However in our study, the simulated ClO mixing ratios underestimate the measurements by a factor of approximately two at 650 K (≈ 26 km altitude).

15 3.3. SZA dependence of simulated ClO to measured ClO

The deviation of simulated ClO ($\text{ClO}^{\text{Model}}$) to measured ClO (ClO^{Meas}) is analyzed as a function of the SZA. For this purpose, the measured ClO mixing ratios were averaged in SZA intervals of 0.5°. The average properties of these SZA intervals are shown in Table 5. To take into account the uncertainties of the model simulations we calculate
20 the ratio $\text{ClO}^{\text{Model}}/\text{ClO}^{\text{Meas}}$ for each model trajectory and for all sensitivity simulations shown in Figs. 6 and 7. A tendency of the ratio $\text{ClO}^{\text{Model}}/\text{ClO}^{\text{Meas}}$ to increase for SZAs larger than 87° is found for the Aire flight (see Fig. 9). For the León flight, we have no ratio of $\text{ClO}^{\text{Model}}/\text{ClO}^{\text{Meas}}$ for SZAs larger than 87°. However, for measurements at 87°, the ratio $\text{ClO}^{\text{Model}}/\text{ClO}^{\text{Meas}}$ is also increased, in contrast to the ratio $\text{ClO}^{\text{Model}}/\text{ClO}^{\text{Meas}}$ at
25 87° for the Aire flight. All other ratios $\text{ClO}^{\text{Model}}/\text{ClO}^{\text{Meas}}$ are in the interval 1.0 ± 0.5 including the discrepancy found in the ClO daylight profile at around 650 K for the León flight. Clearly for SZA larger than 86°–87° the model substantially overestimates the observed ClO mixing ratios. The reason for this is presently not known. Further

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evidences exist that for high solar zenith angles the stratospheric chlorine chemistry is not completely understand. [Rivière et al. \(2003\)](#) reported that the comparison of nighttime balloonborne measurements of OCIO and NO₂ in the Arctic polar vortex with model simulations shows that some uncertainties still exist in the interaction between nitrogen and halogen species.

4. Summary and conclusions

We have presented two balloonborne in situ measurements of ClO conducted in the northern hemisphere midlatitudes stratosphere during the period of the maximum in total inorganic chlorine in the atmosphere. Both ClO measurements were conducted on board the TRIPLE balloon payload launched in November 1996 in León, Spain, and in May 1999 in Aire sur l'Adour, France. For both flights a vertical ClO daylight and night profile could be obtained over an altitude range of approximately 15–31 km.

Using the photochemical box model version of the CLaMS model ([McKenna et al., 2002a,b](#)) simulations along 24-h backward trajectories were presented to study the diurnal variation of ClO in the lower midlatitude stratosphere. The simulations were initialized with all available stratospheric measurements, together with tracer-correlations, and informations deduced from a 2-D model. The flight launched in León is characterized by a more complex dynamical situation (possible contribution of a mix of vortex and non-vortex air) and fewer constraints for the model calculations being available from tracer measurements in contrast to the flight launched in Aire sur l'Adour. For the flight launched in Aire sur l'Adour 1999, the model simulations show a good agreement with the ClO measurements over the entire altitude range of 20–31 km and for both the day and night profile. For the flight launched in León, simulated ClO mixing ratios likewise reproduce the measured ClO mixing ratios, except at around ≈650 K potential temperature (≈26 km altitude), where simulated ClO mixing ratios underestimate measured daylight ClO mixing ratios by a factor of approximately two. A tendency that simulated ClO mixing ratios overestimate measured ClO mixing ratios for SZAs larger

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than 86–87° is found consistently for both flights. In summary, we conclude that no indication can be deduced from the present ClO measurements that substantial uncertainties exist in midlatitude chlorine chemistry of the stratosphere with the exception of SZAs larger than 86–87°.

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Table 1. Sources of the major chemical species used to initialize the model simulations for the flight on 5 May 1999 launched in Aire sur l’Adour and for the flight on 14 November 1996 launched in León.

Species	Aire sur l’Adour 1999	León 1996
CH ₄	cryogenic whole air sampler ^a	HALOE (1–5 Nov. and 15–22 Nov. 1996) ^f
N ₂ O	cryogenic whole air sampler ^a	CH ₄ –N ₂ O correlation ^g
Cl _y	cryogenic whole air sampler ^a	N ₂ O–Cl _y correlation ^h
HCl	HALOE (25–27 April 1999) ^b	HALOE ^f
ClONO ₂	Cl _y –HCl	Cl _y –HCl
ClO	as zero ^c	as zero ^c
NO _y	N ₂ O–NO _y correlation ^d	N ₂ O–NO _y correlation ^d
NO _x = NO + NO ₂	HALOE ^b	HALOE ^f
HNO ₃ + 2 × N ₂ O ₅	= NO _y –ClONO ₂ –NO _x ^e	= NO _y –ClONO ₂ –NO _x ^e
O ₃	ozone sonde ^a	HALOE ^f
H ₂ O	FISH ^a	HALOE ^f
all other	Mainz 2-D model	Mainz 2-D model (Gidel et al., 1983; Grooß, 1996)

^a Conducted on board TRIPLE (cf. Sect. 2). ^b Observations of the Halogen Occultation Experiment (HALOE) on board the UARS satellite (Russell et al., 1993) in northern hemisphere midlatitudes (within 35° N and 50° N) are only available between 25 and 27 April 1999. A mean vertical profile is derived. ^c ClO and all other chlorine species, except ClONO₂ and HCl were initialized as zero. ^d This correlation (Sugita et al., 1998) was derived from measurements by the ATMOS (Atmospheric Trace Molecule Spectroscopy) instrument on board the space shuttle during the ATLAS 3 mission within a period of 10 days in early November 1994. The correlation is valid for high and midlatitudes. ^e As upper and lower limit for the partitioning, we assume a ratio of HNO₃:2 × N₂O₅ of 9:1 (For León: case 1, 2) and of 1:9 (For León: case 3 for midlatitude conditions and case 4 for vortex conditions), respectively. All other species of the nitrogen family were initialized as zero. ^f A mean profile derived from HALOE measurements between 1–5 November and 15–22 November 1996 within 35° N and 50° N for midlatitude (case 1, 3) and vortex (case 2, 4) air masses (cf. Sect. 3.2). ^g A CH₄–N₂O correlation is used derived from measurements of the ATMOS instrument conducted during different missions in March 1992, April 1993, and November 1994 (Michelsen et al., 1998) for midlatitudes (case 1, 4). For vortex conditions (case 2, 4), we employed the CH₄–N₂O correlation (Grooß et al., 2002) to determine N₂O derived from measurements conducted on board the ER-2 aircraft and on board the TRIPLE payload during the Arctic winter 1999/2000 inside the vortex. Above 25 km altitude (the maximum altitude of the TRIPLE flights), a CH₄–N₂O correlation is used derived from ATMOS measurements for polar latitudes (Michelsen et al., 1998). ^h To infer Cl_y, we used for midlatitude and vortex conditions the N₂O–Cl_y correlation derived from measurements of the cryogenic whole air sample on board the TRIPLE payload conducted in Kiruna and in Aire sur l’Adour 1999 (Engel et al., 1999).

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Table 2. Mixing ratios of the major chemical species used to initialize the model simulations for the flight on 5 May 1999 launched in Aire sur l'Adour for the 9th cycle (case a).

THETA	600	600	700	700	800	800	850	850	866	866	875	874	874	871	871
trajno ^a	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15
SAZ ^{a,b}	91.8	70.5	90.4	73.2	88.8	76.3	88.0	79.0	80.0	82.0	83.0	84.0	84.8	86.1	87.0
CH ₄ , ppmv	1.29	1.29	1.01	1.01	0.77	0.77	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Cl ₂ , ppbv	2.11	2.11	2.88	2.88	3.20	3.20	3.32	3.32	3.32	3.32	3.32	3.32	3.32	3.32	3.32
HCl, ppbv	1.37	1.39	1.84	1.85	2.14	2.14	2.26	2.26	2.31	2.38	2.34	2.34	2.34	2.33	2.33
ClO, pptv	2.93	65.50	14.63	99.66	36.35	130.52	52.35	137.90	130.39	113.31	103.25	94.14	85.85	71.96	63.18
ClONO ₂ , ppbv	0.74	0.66	1.02	0.92	1.02	0.92	0.99	0.90	0.86	0.82	0.86	0.87	0.88	0.90	0.91
NO _y , ppbv	7.09	7.09	12.34	12.35	16.01	16.01	16.72	16.73	16.73	16.73	16.73	16.73	16.73	16.73	16.73
NO, ppbv	0.24	0.83	1.44	2.22	2.98	3.76	3.55	4.21	4.34	4.45	4.27	4.19	4.15	3.97	3.88
NO ₂ , ppbv	1.44	0.99	3.03	2.52	4.40	3.96	4.71	4.38	4.46	4.59	4.55	4.57	4.58	4.67	4.74
HNO ₃ , ppbv	3.71	3.79	4.54	4.67	4.09	4.21	3.54	3.59	3.31	2.97	3.14	3.16	3.15	3.19	3.17
N ₂ O ₅ , ppbv	0.40	0.34	1.07	0.93	1.69	1.51	1.90	1.76	1.82	1.90	1.90	1.91	1.93	1.94	1.95
O ₃ , ppmv ^c	4.46	4.46	5.61	5.61	6.36	6.36	6.82	6.82	6.82	6.82	6.82	6.82	6.82	6.82	6.82

^a number of trajectory

^b SAZ at the end of the trajectory

^c initial mixing ratios for all cycles

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Table 3. Mixing ratios of the major chemical species used to initialize the model simulations for the flight on 14 November 1996 launched in León for midlatitude air masses (case 1) and for the 9th cycle.

THETA	500	500	600	600	650	650	700	750	800	800	850	850	900	900
trajno ^a	01	02	03	04	05	06	07	08	09	10	11	12	13	14
SAZ _h ^o ^b	87.1	64.2	84.9	66.4	83.8	67.6	83.1	82.4	81.5	71.0	79.4	73.3	76.0	74.9
CH ₄ , ppmv	1.29	1.29	1.14	1.14	1.13	1.13	1.13	1.11	1.08	1.08	1.02	1.02	0.96	0.96
Cl ₂ , ppbv	1.80	1.80	2.53	2.53	2.57	2.57	2.60	2.67	2.78	2.78	2.97	2.97	3.10	3.10
HCl, ppbv	1.35	1.39	1.64	1.66	1.72	1.73	1.83	1.98	2.15	2.15	2.37	2.37	2.57	2.56
ClO, pptv	9.83	46.94	43.57	118.82	54.84	127.62	59.79	64.42	70.45	130.12	88.49	128.21	113.73	120.94
ClONO ₂ , ppbv	0.43	0.36	0.84	0.73	0.79	0.69	0.70	0.62	0.55	0.48	0.51	0.46	0.42	0.41
NO _y , ppbv	6.38	6.38	10.10	10.10	10.35	10.35	10.56	11.05	11.87	11.87	13.50	13.50	14.78	14.78
NO, ppbv	0.14	0.30	0.40	0.64	0.73	0.98	1.23	1.93	2.98	3.34	4.23	4.55	5.66	5.72
NO ₂ , ppbv	0.23	0.27	0.56	0.70	0.89	1.01	1.31	1.79	2.34	2.39	2.94	2.98	3.43	3.43
HNO ₃ , ppbv	5.34	5.24	7.58	7.40	6.91	6.81	5.90	4.89	3.79	3.80	3.20	3.14	2.46	2.46
N ₂ O ₅ , ppbv	0.09	0.08	0.30	0.26	0.46	0.38	0.66	0.87	1.07	0.90	1.28	1.15	1.38	1.35
O ₃ , ppmv ^c	2.12	2.12	4.54	4.54	5.44	5.44	6.00	6.41	6.66	6.66	6.79	6.79	6.78	6.78

^a number of trajectory
^b SAZ at the end of the trajectory
^c initial mixing ratios for all cycles

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Table 4. Mixing ratios of the major chemical species used to initialize the model simulations for the flight on 14 November 1996 launched in León for vortex air masses (case 2) and for the 9th cycle.

THETA	500	500	600	600	650	650	700	750	800	800	850	850	900	900
trajno ^a	01	02	03	04	05	06	07	08	09	10	11	12	13	14
SAZ ^b	87.1	64.2	84.9	66.4	83.8	67.6	83.1	82.4	81.5	71.0	79.4	73.3	76.0	74.9
CH ₄ , ppbv	1.19	1.19	0.95	0.95	0.84	0.84	0.73	0.64	0.58	0.58	0.55	0.55	0.52	0.52
Cl ₂ , ppbv	2.34	2.34	2.96	2.96	3.14	3.14	3.26	3.31	3.33	3.33	3.33	3.33	3.33	3.33
HCl, ppbv	1.60	1.63	2.04	2.06	2.24	2.26	2.39	2.45	2.49	2.48	2.52	2.52	2.59	2.58
ClO, pptv	15.47	66.49	39.13	100.56	46.97	102.47	54.86	67.65	85.01	157.51	112.75	164.60	155.11	164.97
ClONO ₂ , ppbv	0.73	0.63	0.87	0.78	0.85	0.77	0.81	0.79	0.75	0.67	0.69	0.63	0.58	0.57
NO _y , ppbv	8.96	8.96	13.32	13.32	15.15	15.15	16.39	16.69	16.23	16.23	15.97	15.97	15.68	15.68
NO, ppbv	0.14	0.32	0.64	0.97	1.53	1.93	2.71	3.84	4.86	5.27	5.61	5.94	6.38	6.43
NO ₂ , ppbv	0.27	0.35	0.80	0.94	1.46	1.55	2.17	2.70	3.08	3.13	3.32	3.39	3.52	3.52
HNO ₃ , ppbv	7.50	7.36	10.10	9.85	9.92	9.76	8.83	7.13	5.12	5.11	3.79	3.71	2.64	2.64
N ₂ O ₅ , ppbv	0.12	0.11	0.40	0.34	0.65	0.52	0.90	1.08	1.19	0.99	1.26	1.13	1.26	1.24
O ₃ , ppmv ^c	2.50	2.50	4.03	4.03	4.21	4.21	4.39	4.67	5.07	5.07	5.43	5.43	5.74	5.74

^a number of trajectory
^b SAZ at the end of the trajectory
^c initial mixing ratios for all cycles

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Table 5. Average properties of the SZA intervals for the ClO measurements as shown in Fig. 9.

trajno	SZA ^a	N ^b	$\overline{\text{ClO}}$ [pptv] ^c	S($\overline{\text{ClO}}$) [pptv] ^d	rel. S($\overline{\text{ClO}}$) [%]
Aire sur l'Adour 1999					
1	91.8	18	0.3	0.9	313.3
2	70.5	17	68.7	2.1	3.1
3	90.4	18	6.6	1.4	20.9
4	73.2	16	113.8	4.0	3.5
5	88.8	18	16.5	2.3	13.7
6	76.3	16	157.7	3.8	2.4
7	88.0	18	34.0	3.3	9.8
8	79.0	17	147.9	4.5	3.1
9	80.0	17	140.9	3.5	2.5
10	82.0	17	126.1	3.8	3.0
11	83.0	17	113.4	9.1	8.1
12	84.0	17	96.7	5.1	5.3
13	84.8	14	74.8	7.3	9.7
14	86.1	16	72.4	4.4	6.1
15	87.0	18	58.1	5.2	8.9
León 1996					
1	87.1	18	4.3	1.1	24.2
2	64.2	36	53.4	2.0	3.7
3	84.9	18	33.5	1.8	5.3
4	66.4	30	140.3	1.2	0.9
5	83.8	18	42.3	1.1	2.7
6	67.6	26	170.7	2.2	1.3
7	83.1	18	39.7	1.4	3.6
8	82.4	18	47.9	2.7	5.6
9	81.5	18	65.7	3.9	5.9
10	71.0	23	201.1	2.8	1.4
11	79.4	19	107.4	4.5	4.2
12	73.3	21	172.9	2.4	1.4
13	76.0	19	141.7	8.1	5.7
14	74.9	19	166.2	3.1	1.8

^a Center of the SZA bins of ±0.25°
^b Number of elements within bin
^c Average ClO mixing ratio within bin
^d Standard deviation of the mean: $S(\overline{\text{ClO}}) = \sqrt{\frac{1}{N(N-1)} \sum_{i=1}^N (\overline{\text{ClO}} - \text{ClO}_i)^2}$. The absolute error of $\overline{\text{ClO}}$ is (20–23%), even if $S(\overline{\text{ClO}})$ is lower caused by statistics.

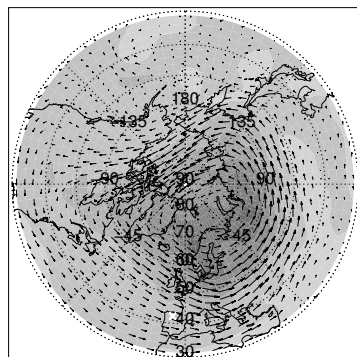
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UKMO Global Model Analysis
VALID AT 12Z ON 14/ 11/ 1996
LEVEL: 700. K

 $10^{(-6)} \text{K}^* \text{m}^2 / (\text{kg}^* \text{s})$

PV

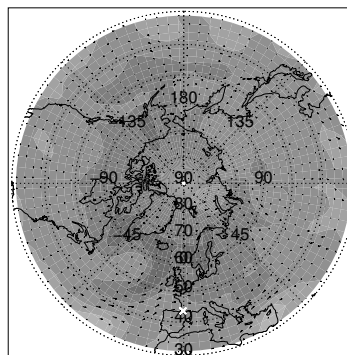


→ represents 50 m/s

UKMO Global Model Analysis
VALID AT 12Z ON 3/ 5/ 1999
LEVEL: 700. K

 $10^{(-6)} \text{K}^* \text{m}^2 / (\text{kg}^* \text{s})$

PV



→ represents 50 m/s

Fig. 1. Potential vorticity ($1 \text{ PVU} = 10^{-6} \text{ K m}^2 \text{ kg}^{-1} \text{ s}^{-1}$) on 14 November 1996 (left panel) and on 3 May 1999 (right panel), 12:00 UT on the 700 K isentropic level derived from data of the UK Met Office (UKMO) analyses. The wind direction is marked by arrows their length being proportional to horizontal wind velocity. The location where the balloon is launched (León, Spain, left panel, and Aire sur l'Adour, France, right panel) is marked by a white cross.

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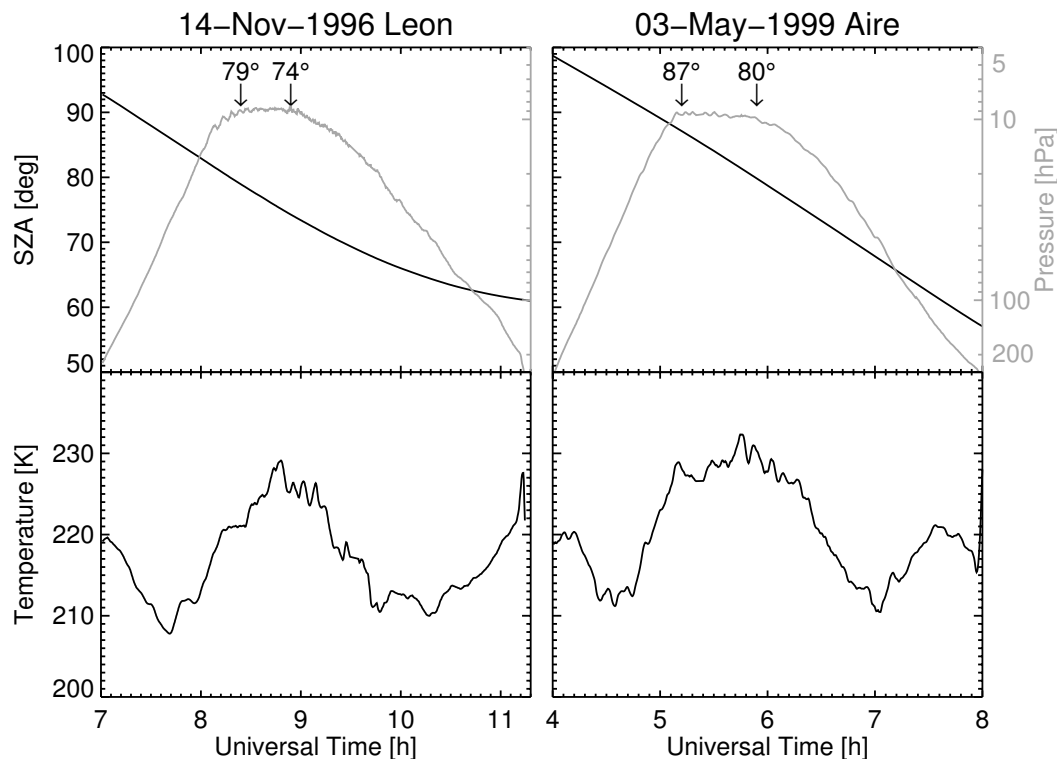


Fig. 2. Meteorological parameters for the flights of the TRIPLE payload on 14 November 1996 (left) and on 3 May 1999 (right) as a function of UT time: Top panel: pressure (gray line) and solar zenith angle (SZA) (black line). Beginning and end of the float is marked by arrows; the corresponding solar zenith angles are also noted. Bottom panel: temperature (black line).

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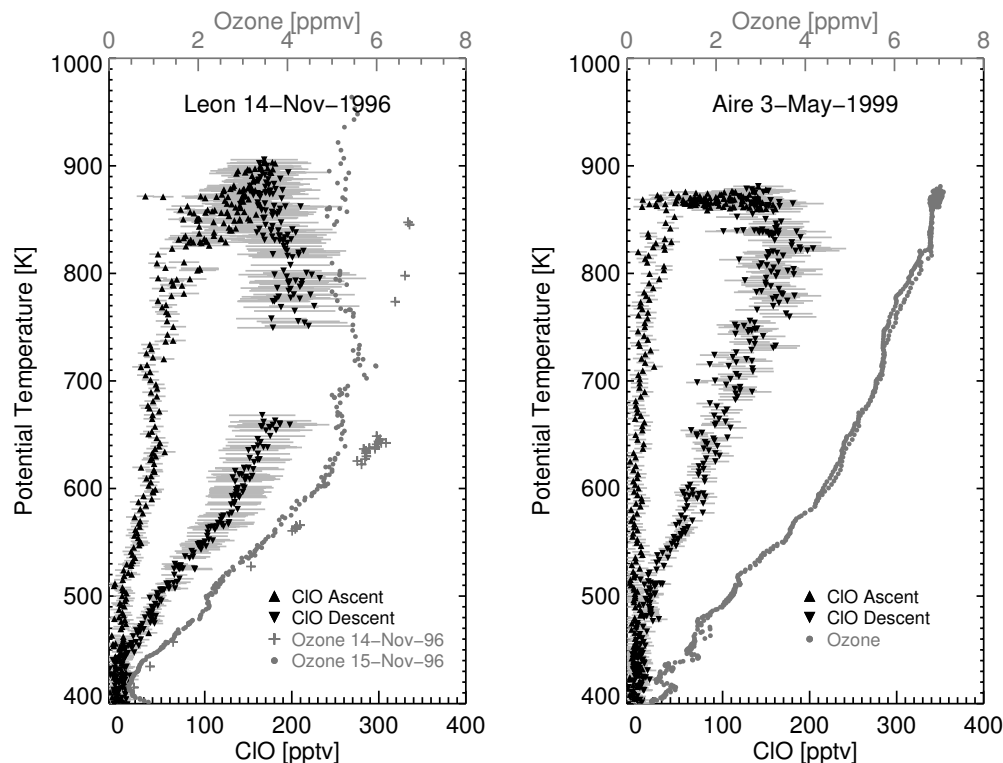


Fig. 3. Measured ClO mixing ratios as a function of the potential temperature of the balloon flights launched on 14 November 1996 in León (left) and launched on 3 May 1999 in Aire sur l'Adour (right). The 1σ accuracy for the ClO measurements is approximately 20–23% (gray bars). For the flight conducted 1996, no data could be obtained at around 720 K caused by a temporary disfunction of the photomultiplier. In addition, for both flights O_3 mixing ratios are shown measured simultaneously by an ECC ozone sonde on board the TRIPLE payload. Because the signal of the ozone sonde was jammed on 14 November 1996, additional ozone measurements are shown conducted by an ozone sonde launched in León on 15 November 1996.

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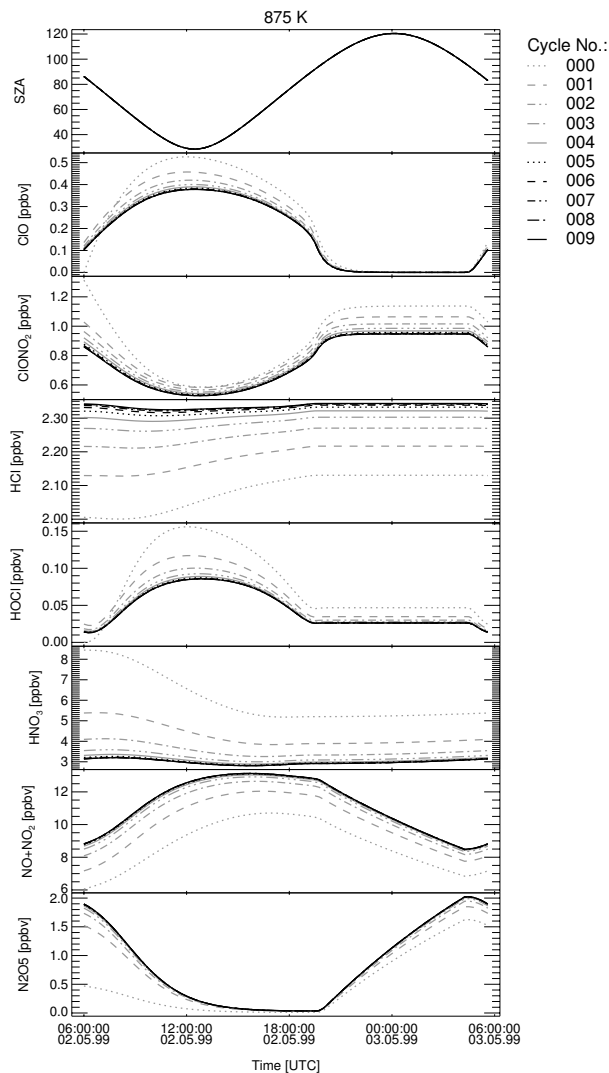


Fig. 4. The convergence of simulated diurnal variation of various species for the cycles 0 to 9 (for case a fixed ozone, see text) are shown at 875 K potential temperature for the flight launched on 3 May 1999 in Aire sur l'Adour.

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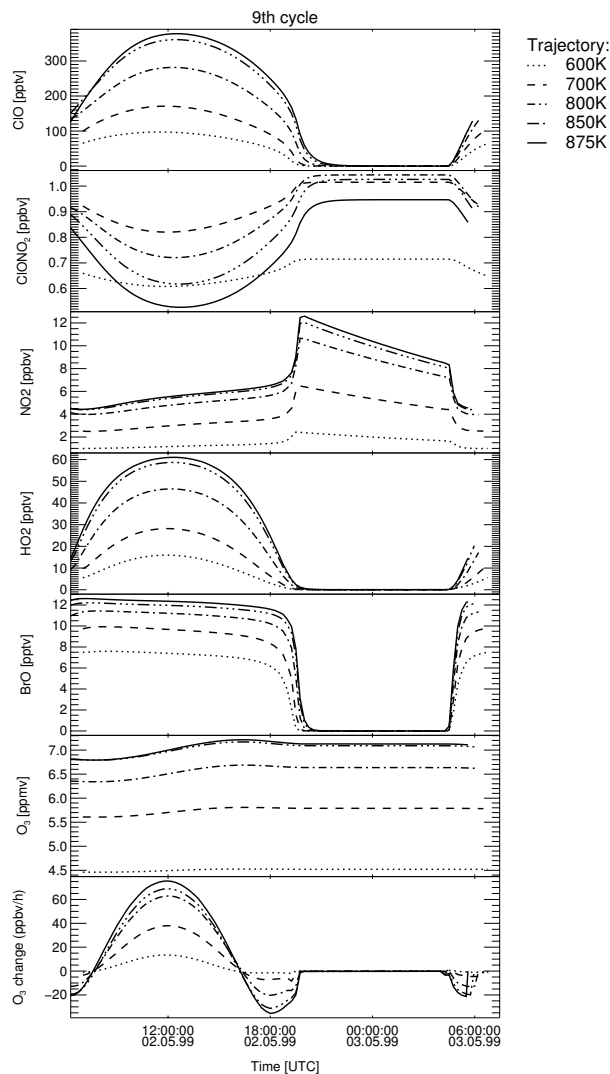


Fig. 5. For the flight launched on 3 May 1999 in Aire sur l'Adour, the simulated diurnal variation of ClO, ClONO₂, NO₂, HO₂, BrO, O₃ mixing ratios, and the ozone change per hour are shown between 600 K and 875 K potential temperature for the 9th cycle (for case a fixed ozone, see text).

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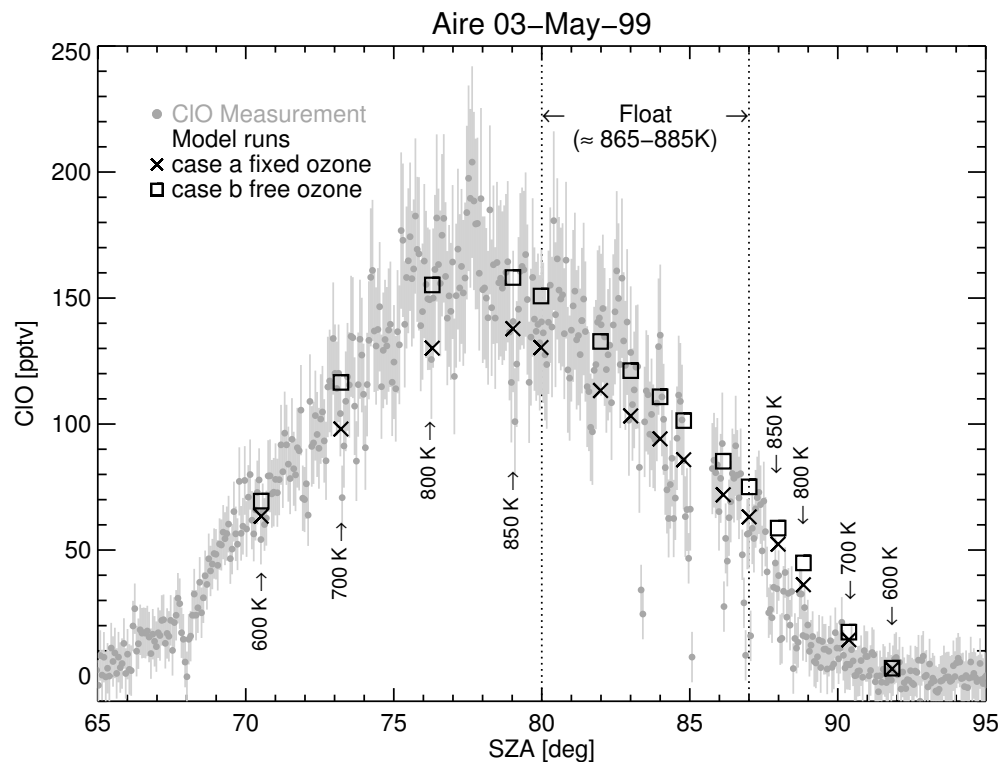


Fig. 6. Simulated ClO mixing ratios as a function of SZA compared to measured ClO mixing ratios of the TRIPLE flight launched on 3 May 1999 in Aire sur l'Adour. The uncertainties of the ClO measurements are shown as gray bars. The chemistry along each 24-h backward trajectory is calculated a few times using the results of the previous model simulation to initialize the following simulation. Here model simulations are shown after 9 such cycles. For details concerning the different model scenarios see text. The corresponding levels of potential temperature are labeled with arrows.

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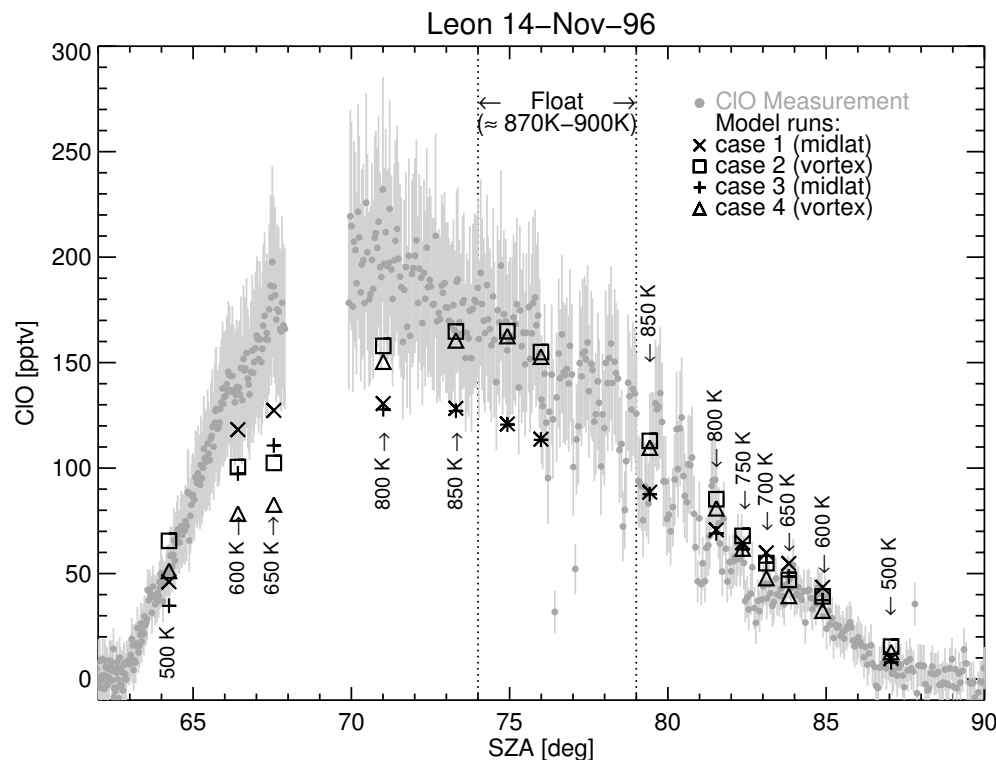


Fig. 7. Simulated ClO mixing ratios as a function of SZA compared to measured ClO mixing ratios of the TRIPLE flight launched on 14 November 1996 in León. The uncertainties of the ClO measurements are shown as gray bars. The chemistry along each 24-h backward trajectory is calculated a few times using the results of the previous model simulation to initialize the following simulation. Here model simulations are shown after 9 such cycles. For case 1 and 2 the model is initialized using a data set representing midlatitude air masses and vortex air masses, respectively (cf. Sect. 3.2). For case 3 and case 4 the NO_y partitioning is changed (cf. Table 1). The corresponding levels of potential temperature are labeled with arrows.

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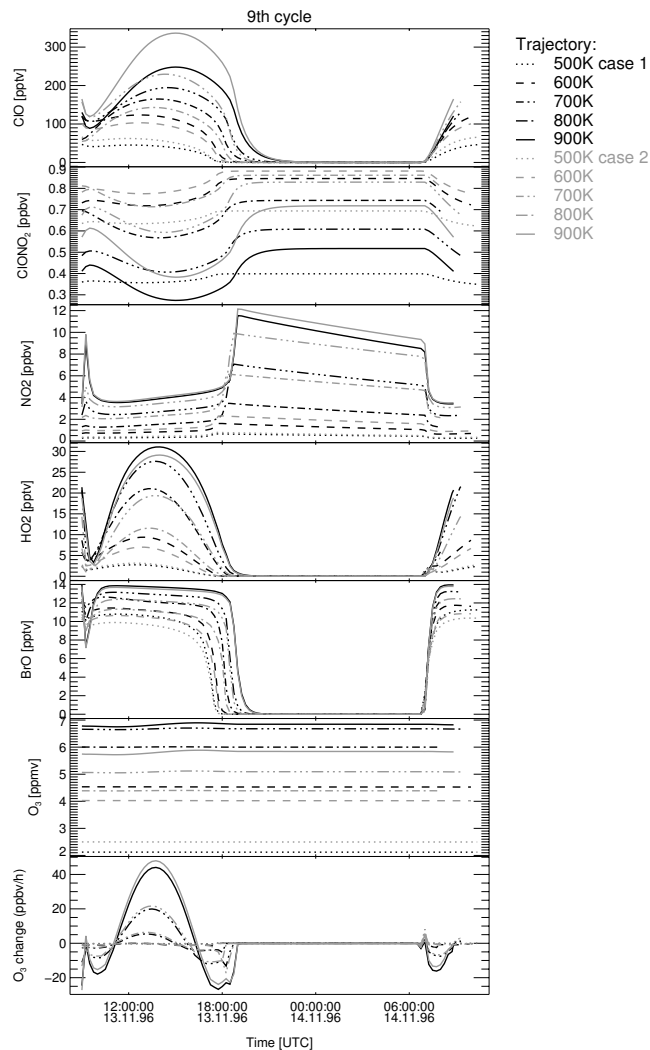


Fig. 8. For the flight launched on 14 November 1996 in León, the simulated diurnal variation for case 1 and 2 of ClO, ClONO₂, NO₂, HO₂, BrO, O₃ mixing ratios, and the ozone change per hour are shown between 500 K and 900 K potential temperature for the 9th cycle.

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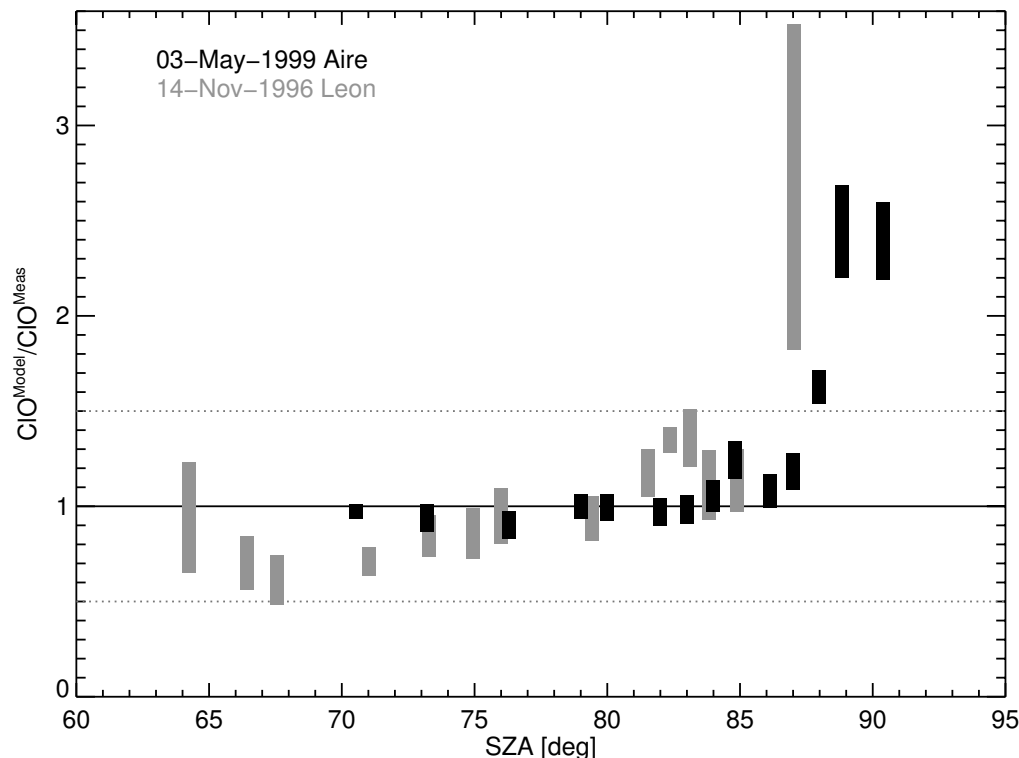


Fig. 9. The ratio of simulated to measured ClO mixing ratios as a function of SZA. The measured ClO mixing ratios are averaged in SZA intervals of 0.5° centered at the SZA endpoint of each trajectory (cf. Table 5). The ratio $\text{ClO}^{\text{Model}} / \text{ClO}^{\text{Meas}}$ is calculated for each model trajectory and for all sensitivity simulations shown in Figs. 6 and 7. The relative measurement error of ClO^{Meas} ($=\text{ClO}$) for 92° SZA for the flight launched in León is very large (cf. Table 5) and is not shown here. All the ratios $\text{ClO}^{\text{Model}} / \text{ClO}^{\text{Meas}}$ are in the interval 1.0 ± 0.5 (dotted line), except for SZAs larger than 86° – 87° .

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