

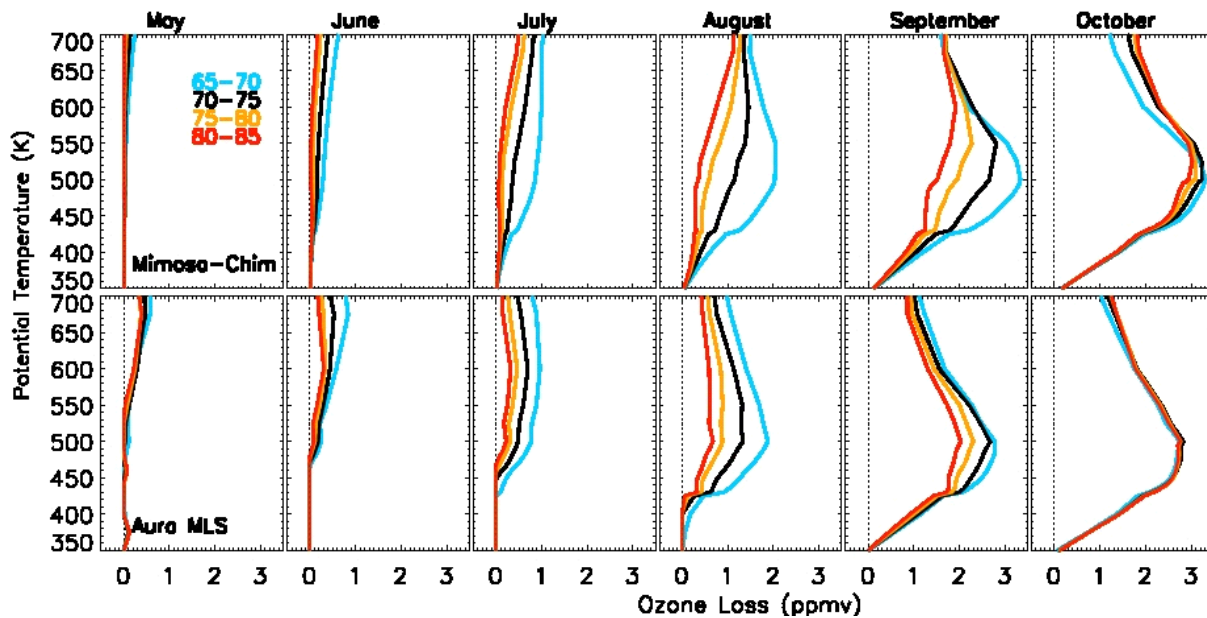
## REPLY TO REFEREE #1

The authors have now clarified and sufficiently addressed the comments and I recommend publication in ACP after some corrections:

Thank you very much for your comments on the manuscript.

1) Figure 1. Do you need to plot every 2 degree averaged equivalent latitude ozone loss profile? I don't think that is necessary.

In contrast to previous studies, we have high resolution measurements and simulations here. In order to take the advantage of those, we have shown highly resolved equivalent latitude bins, as opposed to previous studies on the polar ozone loss. In addition, if we change the figure, we need to completely change the description in that section. To avoid such large changes in the text, we would like to keep this figure in the text. However, we do respect the referee suggestion and we present the 5-degree analysis results here.



2) Figure 2. Y-axis maybe better from 175-210 K. From this plot, it seems that 2013 is the coldest year which is not consistent with the text mentioned in the paper (that 2006 is the most coldest winter).

Done. Please find the new [Figure 2](#). The statement about the “coldest winter” is general, not with respect to the altitude we have shown. Note that the evolution of temperature is different at each vertical level. This has been mentioned in lines 316—319.

3) Fig6, I am not sure how you come out the estimated uncertainty of the column loss is about 10%.

This is based on our error estimation using different passive tracers and measurements for various winters, as presented in Kuttippurath et al. (2011). The estimated uncertainty ranges between 3 and 10% (root sum square), depending on altitude/column range and day of year. Here the difference between measurements and model simulations is slightly larger and hence the upper limit is mentioned. The reference is cited in the [Figure 6 Caption](#).

4) Fig7. There is no point to plot ozone production rate at 500 K since it is negligible.

Done. Please find the new [Figure 7](#).

5) Line 87, The model vertical resolution is 1.5-2 km between 350 and 950 K, how can you say “the simulations are highly resolved in the lower stratosphere (about 0.5 km) too....”?

The vertical resolution of the model between 425 K and 550 K is 5 K, which is roughly 0.5 km.

6) Line 133, reference is needed for REPROBUS CTM.

Done. Please find the reference in [line 136](#)

7) Line 136, add degree symbol for 2x2.

Done. Please find it in [line 139](#).

8) Line 188, change "Ozone Loss=Model Passive Tracer - Ozone (Measured/Simulated)" to "difference between the modeled passive odd-oxygen tracer (defined as the sum of O<sub>3</sub>, O(1D) and O<sub>3</sub>(P)) and measured or simulated ozone)". I don't think you need to repeat all the time Chemical loss (passive ozone minus ozone) later on.

Done. Please find it in [lines 192–194](#). As suggested, we have removed it from other places.

9) Line 218, "is largest at 65-69S Eq)", change "69 to 67" based on the Figure 1.

Done. Please find it in [lines 224–225](#).

10) Line 225, change "550 K" to "500-550 K"

Done. Please find it in [lines 231–232](#).

11) Line 241, change "the same" to "similar amount of"

Done. Please find it in [line 248](#).

12) Line 283, change "Situation" to "Conditions"

Done. Please find it in [line 288](#).

13) Line 494, change "August" to "October".

Done. Please find it in [line 499](#).

## REPLY TO REFEREE #2

The authors have addressed all comments and I appreciate the new figures. However, here are some points that have to be clarified before publishing.

**Thank you very much for your comments on the manuscript.**

From my naive point of view I would say that the ozone loss must be equal to the difference between the change of the passive ozone (over a specific time period) minus the change of the interactive ozone (over the same time period).  $Loss = \Delta O_3(\text{passive}) - \Delta O_3(\text{interactive})$ . If I use the time period = 1 day then I get the cumulative ozone loss over one day in ppmv. However, you use the (daily mean?) ozone fields instead of the ozone tendencies of the two tracers. What is the idea behind this? Or is the passive tracer set equal to the interactive tracer after each time step in the model? Is it possible that the unit is something like the daily mean of the loss in ppmv integrated over a second?

The time step in the model is 15 minutes and we write the output every 6 hr. In order to compare with the measurements, we interpolate these model results (both ozone and passive tracer) with respect to time and location of the measurements, and then find the ozone loss. Since the ozone tendencies are in ppmv, the ozone loss is also in ppmv. The daily average of the ozone loss is computed afterwards (e.g. after individual ozone loss computations for

each measurement in a single day). Please note that the passive tracer is initialized only once at the beginning of the simulation. Therefore, the ozone loss that we find is the cumulative loss in ppmv since the beginning of the simulation. These have been mentioned in [lines 139–144](#).

But if less ozone is transported downward also the descent of the passive tracer is reduced. Doesn't this mean that the measured ozone loss is rather overestimated?

Yes, this has been corrected in [line 471](#).

*Specific comments:*

Line 8: Please remove "that"

Done.

Line 39: .. losses in stratospheric ozone have been ..

Done. Please find it in [line 39](#).

Line 44: ... over the region, the chlorine and bromine induced catalytic ozone loss takes place..

Done. Please find it in [line 44–45](#).

Line 55: .. vortex that forms in fall/winter in the stratosphere is relatively ...

Done. Please find it in [line 56](#).

Line 60: .. and the concomitant stability of the polar vortex ..

Done. Please find it in [line 61](#).

Line 134: Please remove "also"

Done.

Line 136: 2°x2°

Done. Please find it in [line 139](#).

Line 249: Please remove "normal"

Done.

Line 294: .. are higher (around 184 K) than in other winters ..

Done. Please find it in [line 299](#).

Lines 328-332: I suggest moving this sentences a little bit backwards, after the statement that the simulated ClO stands in contrast to the temperature structure.

Done. Please find it in [lines 333–337](#).

Line 362: .. as HCl is smaller in the simulations than in the measurements ..

Done. Please find it in [lines 367–368](#).

Lines 375-377: Slower vertical descent of what? Ozone or chlorine? Since there is an underestimation I guess you mean slower vertical descent of ozone.

**Yes, please find it in [line 382](#).**

Line 418: .. loss onset (i.e. ozone loss > 0.5 ppmv) ..

**Done. Please find it in [line 423](#).**

Line 624: I suggest writing something like the following to get it clarified: ..., "which included an extremely cold winter (2006)...."

**Done. Please find it in [line 628](#).**

Line 645-650: On the one hand there is less chlorine and thus less ozone loss due to the slower descent and on the other hand there is less ozone transported downwards. You should specify in which altitude which process is relevant.

**Done. Please find the altitude information in [lines 651—656](#).**

Line 661-667: .. with a number of winters showing shallow ozone holes, but also with the year of the maximum ozone hole in the last decades.

**Done. Please find it in [lines 669—670](#).**

Figure 2: - Is it possible to change the range of the y-axis to 175 - 215 K? - From the figure, the TICE threshold temperature seems to be 189 K. I thought it is 188 K?

**Done. Please find the new [Figure 2](#). The TICE threshold line is also changed to 188 K.**

# Variability of Antarctic ozone loss in the last decade (2004–2013): High resolution simulations compared to Aura MLS observations

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**Abstract.** A detailed analysis of the polar ozone loss processes during ten recent Antarctic winters is presented with high resolution Mimosa-Chim model simulations and high frequency polar vortex observations from the Aura Microwave Limb Sounder (MLS) instrument. The high frequency measurements and simulations help to characterize the winters and assist the interpretation of interannual variability better than by using either data or simulations alone. Our model results for the Antarctic winters 2004–2013 show that chemical ozone loss starts in the edge region of the vortex at equivalent latitudes (EqLs) of 65–67° S in mid-June/July. The loss progresses with time at higher EqLs and intensifies during August–September over the range 400–600 K. The loss peaks in late September/early October, when all EqLs (65–83°) show similar loss and the maximum loss (> 2 ppmv [parts per million by volume]) is found over a broad vertical range of 475–550 K. In the lower stratosphere, most winters show similar ozone loss and production rates. In general, at 500 K, the loss rates are about 2–3 ppbv sh<sup>-1</sup> (parts per billion by volume/sunlit hour) in July and 4–5 ppbv sh<sup>-1</sup> in August/mid-September, while they drop rapidly to zero by mid-October. In the middle stratosphere, the loss rates are about 3–5 ppbv sh<sup>-1</sup> in July–August and October at 675 K. On average, the Mimosa-Chim simulations show that the very cold winters of 2005 and 2006 exhibit a maximum loss of ~ 3.5 ppmv around 550 K or about 149–173 DU over 350–850 K, and the warmer winters of 2004, 2010, and 2012 show a loss of ~ 2.6 ppmv around 475–500 K or 131–154 DU over 350–850 K. The winters of 2007, 2008, and 2011 were moderately cold and thus both ozone loss and peak loss altitudes are between these two ranges (3 ppmv around 500 K or 150 ± 10 DU). The modeled ozone loss values are in reasonably good agreement with those estimated from Aura MLS measurements, but the model under-

estimates the observed ClO, largely due to the slower vertical descent in the model during spring.

## 1 Introduction

Since the early 1980s significant losses in **stratospheric** ozone have been observed in the Antarctic spring (WMO, 2014). The low temperatures (below 195 K) in the polar winter induce the formation of polar stratospheric clouds in the 15–21 km altitude region, on which chlorine and bromine are activated; when the sun returns over the region, **the chlorine and bromine induced catalytic** ozone loss takes place. Since the 1970s, anthropogenic activities gradually increased the concentrations of ozone depleting substances (ODSs) in the atmosphere including chlorine and bromine containing compounds until they peaked around 2000 in the polar regions. The springtime ozone loss, therefore, correspondingly increased since the late 1980s and saturated by the late 1990s (WMO, 2014). In the southern hemisphere, the land and ocean contrast is smaller than in the northern hemisphere, and hence, the generation and propagation of large amplitude planetary waves are not very effective. Therefore, the polar vortex that forms in fall/winter **in the stratosphere** is relatively undisturbed and stable, and typically lasts for more than seven (May–November) months. These dynamical conditions further aggravate the ozone loss in the southern polar vortex region. Because of the suppressed wave and dynamical disturbances, and **the concomitant** stability of the polar vortex, the inter-annual variation in Antarctic ozone loss since the 1990s has been small.

Large variability in Antarctic ozone loss has been seen in the last few years (2004–2013) relative to other winters since 1992 (e.g. Tilmes et al., 2006; Huck et al., 2007; Yang et al., 2006; Santee et al., 2008a). For instance, the winters 2004, 2010, and 2012 were relatively warm with minor warmings and hence, limited ozone loss (Santee et al., 2005; de Laat

and van Weele, 2011; WMO, 2014). The first fortnight of August 2005 was unusually cold and showed a high rate of ozone loss and an unprecedented ozone hole (WMO, 2014). The winter of 2006 was one of the coldest and hence, the Antarctic vortex experienced the largest ozone hole to date (Santee et al., 2011; WMO, 2014). The winters 2007, 2009, and 2013 were characterized by average temperatures and hence, ozone holes of moderate size (Tully et al., 2008; Kuttippurath et al., 2013). However, the winters 2008 and 2011 were again very cold and characterized by large ozone holes (Tully et al., 2011; WMO, 2014). Here, we provide a detailed view of these ten winters in relation to polar processing and the chemistry of ozone loss. In this study, we discuss (i) the interannual variability of ozone loss and chlorine activation, and (ii) horizontal, vertical, and seasonal variability of ozone loss in the Antarctic stratosphere during these (2004–2013) winters. We use high resolution simulations for analysing the polar processing and interannual changes in ozone loss in detail. Note that the simulations are highly resolved in the lower stratosphere (about 0.5 km between 425 and 550 K) too, to closely study the ozone loss features in those peak ozone loss altitude layers. Additionally, the past ten winters offer a good opportunity to test the chemical and dynamical processes in numerical models. Furthermore, observations from the Aura Microwave Limb Sounder (MLS) (Froidevaux et al., 2008; Santee et al., 2008b), one of the best satellite instruments currently available for sampling polar vortices, are compared to the model results. Therefore, for the first time ozone loss and chlorine activation can be studied with high resolution measurements having very good spatial and temporal coverage inside the Antarctic vortex. Previous satellite measurements were relatively limited to a small temporal and spatial area as far as high latitude observations are concerned (e.g. Tilmes et al., 2006; Hoppel et al., 2005). While the Upper Atmosphere Research Satellite MLS (Waters et al., 1999) had a similar latitudinal coverage, the frequency of its polar measurements was lower than that of Aura MLS (e.g. Livesey et al., 2013; Froidevaux et al., 2008). Therefore, the study with high resolution simulations (both horizontally and vertically) together with the high resolution measurements offers some new insights into the polar processing and ozone loss features of the Antarctic stratosphere.

In this article, the Mimosa-Chim chemical transport model (CTM) (e.g. Kuttippurath et al., 2010; Tripathi et al., 2007) is used to simulate the chemical constituents for the period 2004–2013. The simulated results are then compared to the Aura MLS measurements. We first look at the ozone loss evolution within different equivalent latitudes (EqLs) averaged over ten winters in Sect. 3.1. The assessment of the interannual variability of the ozone loss, chlorine activation, and ozone loss rates during the ten (2004–2013) winters is presented in Sect. 3.2. Finally, Sect. 4 concludes with our main findings.

## 2 Simulations and measurements

We use the high resolution Mimosa-Chim CTM for the simulations of chemical constituents (e.g. Kuttippurath et al., 2010; Tripathi et al., 2007). The model extends horizontally from 10° N to 90° S with 1° × 1° resolution, and there are 25 isentropic vertical levels between 350 and 950 K with a resolution of about 0.5–2 km, depending on altitude. The model is forced by European Centre for Medium-Range Weather Forecasts (ECMWF) operational analyses. The vertical levels of this dataset have been changed from 60 to 91 levels from February 2006 to May 2013 and then to 137 levels from June 2013 onward. The chemical fields used to initialize Mimosa-Chim each year are obtained from a long-term simulation of the REPROBUS CTM (Lefèvre et al., 1994) driven by the same ECMWF analyses. The REPROBUS model is equivalent to a lower resolution version of the Mimosa-Chim model, with its resolution being 2° × 2°. The chemical tendencies are calculated every 15 minutes and the output is written for every 6 hr. The passive tracer is initialized only once at the beginning of the simulation and thus the ozone loss is the cumulative loss in ppmv since the beginning of the simulation. The Mimosa-Chim CTM uses the MIDRAD radiation scheme (Shine, 1987). Climatological H<sub>2</sub>O and CO<sub>2</sub>, but interactive O<sub>3</sub> fields are used for the calculation of heating rates. The kinetics data are taken from Sander et al. (2011), but the Cl<sub>2</sub>O<sub>2</sub> photolysis cross-sections from Burkholder et al. (1990), with a log-linear extrapolation up to 450 nm (Stimpfle et al., 2004). These cross-sections are in good agreement with the recent Cl<sub>2</sub>O<sub>2</sub> measurements by Papanastasiou et al. (2009), which form the basis for the JPL 2011 recommendations (i.e. Sander et al., 2011). For each Antarctic winter the model was run from 1 May to 31 October.

The model has detailed polar stratospheric cloud (PSC) formation and growth and sedimentation schemes. The saturation vapor pressure provided by Hanson and Mauersberger (1988) and Murray (1967) is used to assume the existence of Nitric Acid Trihydrate (NAT) and ice particles, respectively. Liquid supercooled sulphuric acid aerosols, NAT, and ice particles are considered in equilibrium with the gas phase (Lefèvre et al., 1998). Equilibrium composition and volume of binary (H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O) and ternary (HNO<sub>3</sub>–H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O) droplets are calculated using an analytic expression given by Carslaw et al. (1995). For NAT and ice particles, the number density is set to 5 × 10<sup>-3</sup> cm<sup>-3</sup>, and the particle diameter is calculated within the scheme from the available volume of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. A denitrification scheme is also incorporated to diagnose the sedimentation of HNO<sub>3</sub> containing particles. In this scheme, the NAT particles are assumed to be in equilibrium with gas phase HNO<sub>3</sub>. All three types of NAT, ice, and liquid aerosol particles are considered, and the sedimentation speed of the particles is calculated according to Pruppacher and Klett (2010).

We use the Aura MLS measurements version (v) 3.3

(Livesey et al., 2013) to compare with simulations. The ozone measurements have a vertical resolution of 2.5–3 km over 215–0.02 hPa, and the vertical resolution of ClO measurements is about 3–3.5 km over 100–1 hPa. The time resolution of the measurements is about 3500 profiles per day. The estimated uncertainty of typical ozone and ClO retrievals is about 5–10 and 10–20 %, respectively (Livesey et al., 2013; Santee et al., 2008a; Froidevaux et al., 2008). To compare with the measurements, the model results (6 h output) are interpolated to the measurement locations.

### 3 Results and discussion

The passive tracer method is applied to compute the ozone loss from the simulations and measurements. This requires simulation of passive ozone (or a passive model tracer), i.e. ozone simulations without interactive chemistry. The “ozone loss” is computed as difference between the modeled passive odd-oxygen tracer [defined as the sum of  $O_3$ ,  $O(1D)$  and  $O_3(P)$ ] and measured or simulated ozone. To derive the ozone loss inside the vortex, we use a vortex edge criterion of 65° EqL. The following equation is used to derive the vortex averaged ozone loss rates and production rates from the model results.

$$\overline{\delta O_3(\theta, j)} \quad (ppbv/sh) = \frac{\sum_{\lambda_{eq}=65}^{\lambda_{eq}=90} \delta O_3(\theta, j, \lambda_{eq}) \times sh(\theta, j, \lambda_{eq})}{\sum_{\lambda_{eq}=65}^{\lambda_{eq}=90} sh(\theta, j, \lambda_{eq})}$$

where,  $\overline{\delta O_3(\theta, j)}$  is the ozone loss or production averaged within EqL ( $\lambda_{eq} \geq 65^\circ$ ) for each model vertical level ( $\theta$ ) and day ( $j$ ).  $\delta O_3(\theta, j, \lambda_{eq})$  is the instantaneous ozone loss or production calculated by the model for each grid point defined by latitude ( $\phi$ ) and longitude ( $\psi$ ) for each  $\theta$  and  $j$ .  $sh(\theta, j, \lambda_{eq})$  is the sunlit hour calculated with respect to solar zenith angle  $< 95^\circ$  that varies between 0 and 1 for complete darkness to full illumination. The  $\lambda_{eq}$  is computed for each model grid point ( $\theta, \phi, \psi$ ) and for each day using potential vorticity (PV) data.

#### 3.1 Ozone loss: the 2004–2013 average

To elucidate various chemical ozone loss features, we analyse the vertical distribution of the average loss in 2004–2013 for different EqL bins estimated from the model and MLS data from May to October, and shown in Fig. 1. The EqL-based analyses extend from 65 to 83° S in 2° increments as calculated for the MLS measurements. A detailed discussion on the calculation of EqLs and determination of the polar vortex edge can be found in Nash et al. (1996) and references therein. The simulations show that the chemical loss starts at lower EqLs of 65–67° S at the edge of the Antarctic vortex

in May, above 600 K, as also shown by Lee et al. (2000), Godin et al. (2000), and Roscoe et al. (2012). It moves down to the lower altitudes by July, and the loss is largest at 65–67° S EqL. The loss continues to increase in August, with the EqLs of 65 and 83° S showing the largest and smallest loss, respectively, in accordance with the increase in incidence of sunlight over the region. A clear difference in the amount of ozone loss estimated at different EqLs is well simulated. At the edge of the vortex, maximum modeled ozone loss of 2.1 ppbv (parts per million by volume) is found around 500–550 K, while in the 70–80° S EqL range the peak loss is found above 600 K.

The ozone loss continues through to September, when all EqLs show large loss. The largest modeled loss is still found in the lower EqLs of 65–69° S, reaching about 3 ppbv at 500 K. The higher EqLs (77–83° S) show the smallest ozone loss and it peaks in the middle stratosphere (600 K), while other EqLs show their peak loss below 575 K. Above 600 K, all EqLs show similar ozone loss of about 1.4 ppbv. The maximum loss is about 3 ppbv at 65–70° S at 500 K, 2.5 ppbv at 70–75° S at 550 K, 1.7 ppbv at 75–80° S at 575 K, and 1.3 ppbv over 80–83° S at 600 K, and thus, the altitude of maximum loss increases with EqL up to September. As expected, the maximum ozone loss is found in October, and all EqLs show more or less the same loss (about 3 ppbv) at the peak loss altitude of around 500 K. In addition, all EqLs show more or less similar amount of ozone loss with altitude below 500 K in October. Above 500 K, the ozone loss shows slight differences, with the largest loss occurring at the highest EqLs, unlike in months earlier than September. Note that the ozone loss presented here is the monthly mean ozone loss, not the instantaneous loss (see later analyses in Sect.3.2.3 and Sect.3.2.5), which explains the large ozone loss estimated for late September and October after the chlorine activation period (mid-June to mid-September). In addition, in October, the mixing processes affecting the airmass within the vortex, when the ozone loss cycles are stopped, also homogenize the ozone distributions.

The analyses with model results below 500 K are in good agreement with those of the MLS measurements. Nevertheless, the loss estimated from the observations is more compact with altitude in October, and the model–measurement differences are relatively larger in September than in other months. The comparison of ozone loss above 550 K shows that the model overestimates the ozone loss there. The ozone loss of about 0.05–0.08 ppbv that is derived from the measurements in May at 360–370 K is within the estimated error bars of the measurements and therefore insignificant. The differences between measurements and simulations will be discussed further in Sect. 3.2.2.

#### 3.2 Interannual variations

We have discussed the general features of the measured and modeled ozone loss evolution in the Antarctic stratosphere.

275 Now we look into the details of the interannual variations in Antarctic ozone loss. It is well-known that low temperatures initiate PSC formation, enabling chlorine activation which then triggers ozone loss. Therefore, we first analyse the minimum temperature and meteorological situation of each winter in 2004–2013. The link between the prevailing meteorology and chlorine activation of the winters is discussed in the following section, as the amount and extent of activated chlorine are a good indicator of the yearly changes in ozone loss. The year-to-year changes in ozone loss, i.e. the vertical profile of ozone loss, column ozone loss, and the instantaneous ozone loss are discussed in detail with respect to the aforementioned factors in the succeeding sections.

### 3.2.1 Meteorological Conditions

Figure 2 shows the minimum polar cap ( $50\text{--}90^\circ$ ) temperature extracted from the ECMWF operational analyses for each winter since 2004 at 500 K ( $\sim 19$  km) potential temperature. In general, the winters show a minimum temperature of about 179–186 K from mid-June to mid-September. Among the winters, 2004 shows relatively higher minimum temperatures in the range of 184–200 K from August onward, although some days can be exempted. In 2005, the temperatures are relatively low and remained around 182 K in July–September, although a minor warming is evident in June. In 2006, the temperatures are higher (around 184 K) than in other winters in late June and July, but the September and October temperatures (183–199 K) are very low. In 2007, 2008 and 2009, the evolution of temperature is very similar, but there are minor differences in the detail, such as a burst of about 181–183 K in July in 2007. In 2010, minor warmings are apparent in early August (182–186 K) and mid-September (185–190 K). The lowest mid-August to October temperatures at this level are found in 2011 as in the case of 2006, but the highest temperatures in October are found in 2012 with values of 194–212 K. In addition, the winter 2013 shows the lowest July–August temperatures, with about 177–179 K. In brief, the winters 2004, 2010 and 2012 can be roughly termed as warm winters (de Laat and van Weele, 2011), and 2005, 2006, 2011, and 2013 cold or very cold winters (WMO, 2014). Since the temperature evolution is between these extremes, the other winters can be called as moderately cold or moderately warm. Note that the winters are categorised with respect to the temperature evolution at this particular potential temperature and hence the classification can be slightly different at other altitude levels. Further details about the temperature distribution and meteorology of the winters 2010–2013 can be found in WMO (2014).

### 3.2.2 Activated Chlorine

Figure 3 compares the simulated and measured ClO at the MLS sampling points inside the vortex, defined here by the area within  $65\text{--}90^\circ$  S EqL, and with solar zenith angle (SZA)

less than  $89^\circ$  as available, for the Antarctic winters 2004–2013. In Mimosa-Chim, relatively high chlorine activation is found in 2005, when a maximum of 1.6–1.8 ppbv (parts per billion by volume) is simulated from June to late July and early August, consistent with the lower temperatures in that winter (WMO, 2014). The other winters show a more or less similar distribution of ClO and thus, chlorine activation, except in the warm winters of 2010 and 2012. The simulated ClO stands in contrast to the temperature structure and PSC observations in each winter (Pitts et al., 2009), which showed the largest areas of PSCs in the coldest winters of 2005 and 2006. It should be noted that chlorine activation does not depend only on temperature and the occurrence of PSCs, but also on the available chlorine reservoirs, which vary from one year to the other (Strahan et al., 2014). However, when we examine the MLS measurements, they mostly follow the temperature history of each winter, as the observations show the strongest chlorine activation in 2005 and 2006, and the weakest in 2010 and 2012. The highest ClO values ( $> 1.5$  ppbv) are found from July to the end of September over 450–600 K in the colder winters, but around 550 K episodically in July–August in the warmer winters in the observations. Therefore, in contrast to the model results, the vortex averaged MLS measurements display a clear interannual variation in the chlorine activation. These comparisons show that the model underestimates the observed ClO over the 450–600 K range.

In order to find out the reasons for the differences between simulated and measured ClO, we compared the simulated HCl,  $\text{N}_2\text{O}$ , and  $\text{HNO}_3$  with the MLS observations. Figure 4 illustrates the ten year average of the vortex mean (defined by  $\geq 65^\circ$  EqL) ClO, HCl,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$  and ozone loss from the Mimosa-Chim model and MLS measurements. The  $\text{N}_2\text{O}$  comparisons show that the simulated values are higher than the measured ones, as illustrated by the 50 and 100 ppbv isopleths. This bias in the simulations implies that the vertical diabatic descent in the model is slower than that deduced from MLS observations in polar spring. Consequently, the  $\text{Cl}_y$  and thus ClO in the model are relatively smaller. Therefore, the available chlorine/HCl for converting to activated ClO is smaller in the model. The HCl comparison corroborates this feature of the simulations, as HCl is smaller in the simulations than in the measurements in early and middle winter, and in late spring in the lower stratosphere. The deficiency in the vertical descent in the model has clearly affected the ozone simulations. For instance, the statistics of the ozone comparison reveal that the differences in May are negligible at all altitudes. In June–August, the model underestimates the measured ozone by about 0.2–0.5 ppmv below 500 K. In September–October, the model overestimates (0.2–0.4 ppmv) the measured ozone below 450 K, with a peak at around 400 K. However, this overestimation is well below the peak ozone loss altitudes. Above 500 K, the model consistently underestimates the measured ozone from about 0.2 ppmv in June to 0.5–1 ppmv in August–October. Hence



the differences at these altitudes also are qualitatively consistent with the slower vertical descent of ozone in the model. 435

A simulation with a different  $\text{Cl}_2\text{O}_2$  recombination rate constant, Nickolaisen et al. (2006) instead of the JPL recommendation, as suggested by von Hobe et al. (2007), was performed to test the sensitivity of the simulations and to diagnose whether the new simulations reduce the model-measurement differences. However, the ClO results did not improve significantly and hence the original simulations are presented. The  $\text{HNO}_3$  comparisons also point out that the denitrification in the model is overestimated, due to the equilibrium PSC scheme of the model, as it forms large NAT particles too readily causing more sedimentation of PSCs and thus more denitrification. 385 390 445

Note that the relatively low model top could also influence the slower descent or vertical transport in the model. A detailed discussion on the differences in measured and modeled ClO and HCl, chlorine partitioning in the model, and the influence of the lower model top in the simulated results will be presented in a separate paper. Also, there can be small interannual differences in the diabatic descent, depending on the accuracy of the wind fields. These have to be kept in mind while interpreting the simulations. However, in a similar study, Santee et al. (2008a) compared the MLS measurements to SLIMCAT model (Chipperfield, 1999) results and found that their simulations slightly overestimate the ClO measurements for the Antarctic winters 2004 and 2005. They attributed these differences to the equilibrium PSC scheme of the model. In contrast, our model ClO results underestimate the observations, although using a very similar PSC scheme in the model. It suggests that even if the models use similar PSC schemes, the difference in model dynamics can induce significant changes in the simulated results. Nevertheless, note that the model has performed better in northern hemispheric simulations, where the ClO simulations overestimate the MLS measurements in the 2011 winter (Kuttippurath et al., 2012), but slightly underestimate them in 2005–2010 (Kuttippurath et al., 2010). 395 400 450 455 460 465 470

### 3.2.3 Ozone loss: vertical and temporal features

Figure 5 shows the vortex averaged ozone loss estimated from the model and MLS at the MLS sampling locations inside the vortex in 2004–2013. As discussed in Sect. 3.1, the ozone loss onset (i.e. ozone loss > 0.5 ppmv) in the model occurs in mid-June at altitudes above 550 K and gradually moves down to the lower stratosphere by mid-August. The loss intensifies by mid-August, peaks by late September/early October and slows down thereafter as the ozone recovers through dynamical processes. 420 475 480

In the simulations, as expected, the colder winters of 2005 and 2006 show early onset of ozone loss, in mid-June. The estimated loss is less than 0.5 ppmv above 675 K until mid-August, increases to 1–1.5 ppmv by mid-September in the lower stratosphere, and peaks at 2.5–3.6 ppmv over 450–

600 K by early October, consistent with the temporal and vertical extent of activated ClO in these winters. A maximum ozone loss of around 3.5 ppmv is derived around 550 K in 2005–2006 and about 3 ppmv around 500 K in 2007, 2008 and 2011. Smaller ozone loss is found in the warmer winters of 2004, 2010 and 2012, where the peak loss is about 2.6 ppmv, around 475 K. A similar range of ozone loss, but in a slightly broader vertical extent of 450–600 K, is simulated in 2009 and 2013. Therefore, the center of the peak ozone loss altitude (i.e. loss > 2 ppmv) also shows corresponding variations in agreement with the meteorology of the winters, as it is located around 550 K in very cold winters (e.g. 2005 and 2006), around 500 K in moderately cold winters (e.g. 2007), and around 475 K in warm winters (e.g. 2004 and 2012).

In general, the timing and vertical range of ozone loss in the simulations are similar to those of the observations. The modeled ozone loss onset is in mid-June, except for the colder winters (when it is in mid-May), as discussed previously, and the loss strengthens by August–September and reaches a maximum in early to mid-October, consistent with those of the observations. The large ozone losses observed above 550 K in September–October in the colder winters (e.g. 2005, 2006, 2007, 2008, and 2011) are also reproduced by the model. In contrast to the observed loss, the simulated ozone loss in 2007 is slightly higher than that of 2005, consistent with the temperature during these years at 500 K. However, the model consistently overestimates the measured ozone loss in the middle stratosphere in all years by about 0.2–0.5 ppmv in spring, as the model underestimates the measured ozone by the same amount at these altitudes, primarily due to the slower descent in the model during the period as discussed before. Therefore, the interannual variations are more prominent in the measurements than in the model simulations. It must be kept in mind that since the same passive model tracer affected by the slower diabatic descent in spring is used to derive ozone loss from the measurements, the measured ozone loss is also overestimated. Both the simulations and the measurements, however, provide consistent results for the peak ozone loss altitudes in each winter.

The ozone loss derived from the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographyY (SCIAMACHY) (Bovensmann et al., 1990) ozone profiles using the vortex descent method shows comparable values to that of the simulations/MLS data for the Antarctic winters 2004–2008 (Sonkaew et al., 2013). There is also good agreement in peak ozone loss values (around 3–3.5 ppmv) and the differences in the altitudes of maximum loss for various winters, as discussed previously for the modeled/MLS ozone loss. In addition, the large loss above 500 K found in the model/MLS data is also inferred from the SCIAMACHY measurements.

### 3.2.4 Partial column ozone loss

In order to gain further insights into the interannual variability of ozone loss, we now analyse the column ozone loss derived from simulations and measurements. Since there are also other published results available for comparisons, analysing partial column loss will assist the interpretation of interannual changes. We have calculated the column ozone loss from the simulations and observations at the MLS footprints inside the vortex for each winter for the complete altitude range of the model and for the altitude region over which peak loss occurs (400–600 K); results are given in Fig. 6. The ozone loss computed are the average over the maximum loss period in the Antarctic; from late September to early October (25 September – 5 October). The simulated results show the lowest ozone loss in 2004 and the highest in 2005 at 350–850 K, depending on the meteorology and chlorine activation during the winters. However, it has to be noted that the ozone hole in 2006 was record-breaking, but both the model simulations and measurements show only slightly lower total column ozone loss compared to 2005, due to the comparatively larger chlorine activation in early winter in 2005, as also illustrated in Fig. 3 (see the difference in chlorine activation in 2006 and 2005). Large ozone loss of about 167 DU is also simulated in the winter 2007 due to relatively strong chlorine activation in that winter (Fig. 3). The other winters show a column ozone loss of about  $155 \pm 10$  DU over the same altitude range. On the other hand, the ozone loss derived from MLS observations shows the highest column ozone loss of about 162–166 DU in the very cold winters of 2005 and 2006, and the lowest of around 127–134 DU in the moderately cold winter of 2013 and the warm winters of 2010 and 2012 at 350–850 K, and these are in agreement with the meteorology of the winters. Despite the differences in the values, the ozone column loss computed for 400–600 K also shows similar patterns as those discussed for the 350–850 K range. Note that there was strong and prolonged chlorine activation in the coldest winter 2006 (i.e. CIO was enhanced slightly longer in this winter than in most other winters). Also, Santee et al. (2011) showed that there was unusually strong chlorine activation in the lowermost stratosphere (around 375 K) that contributed to the record-setting ozone hole/loss in that winter. Therefore, the data exhibit a clear interannual variation of ozone column loss as discussed for the ozone loss profile comparisons in Sect. 3.2.3.

The average partial column ozone depletion above the 550 K level computed from the model and data for the ten winters is about  $50 \pm 5$  DU. This column ozone loss has to be considered when deriving partial column loss from profiles. This is slightly different from the Arctic, where significant ozone loss occurs mostly in the lower stratosphere over 350–550 K in colder winters, and where the depletion above 550 K is limited to  $\sim 19 \pm 7$  DU (Kuttippurath et al., 2010). The larger Antarctic ozone column loss contribution from higher altitudes (above 550 K) is consistent with the

loss estimated above those altitudes, as shown by the ozone profiles in this study for 2004–2013, and in Lemmen et al. (2006) and Hoppel et al. (2005) for a range of Antarctic winters prior to 2004. It is also evident from the maximum ozone loss altitudes, as most Antarctic winters have their peak loss altitudes around 525 K as opposed to 475 K in the Arctic (e.g. Kuttippurath et al., 2012; Tripathi et al., 2007; GroöB et al., 2005b; Rex et al., 2004).

The partial column loss estimated from the Halogen Occultation Experiment ozone measurements ( $\sim 172$  DU) over 350–600 K (Tilmes et al., 2006) is larger than our results for 2004. Our loss estimates over 350–850 K for 2004–2010 are in reasonable agreement with those derived from ground-based and other satellite total ozone observations in the Antarctic (Kuttippurath et al., 2013). The ozone loss computed from a bias-corrected satellite data set using a parameterized tracer by Huck et al. (2007) for the winter 2004 also shows a similar estimate. The slight differences amongst various ozone loss values can be due to the differences in the altitude of ozone loss estimates, vortex definition, vortex sampling, and the method used to quantify the loss by the respective studies.

### 3.2.5 Ozone loss and production rates

The interannual variability of ozone loss is further analyzed with the ozone loss and production rates in the model simulations. Figure 7 shows the instantaneous loss and production rates at 675 and 500 K. In general, at 500 K, the loss rates are about 2–3 ppbvsh<sup>-1</sup> (ppbv/sunlit hour) in mid-June during the onset of ozone loss, about 3–4 ppbvsh<sup>-1</sup> in July as the loss advances to the vortex core (i.e. inside the vortex at higher EqLs) and about 4–5 ppbvsh<sup>-1</sup> from August to mid-September during the peak loss period. The loss rates decrease from late September onward and reach zero by mid-October, and stay at near-zero values thereafter. Since the loss rate during the mid-September to October period depends on photochemical ozone production and loss, interannual variability is small in that period, and most winters show loss rates of about 2–5 ppbvsh<sup>-1</sup>. However, significant year-to-year variations are noted from mid-June to mid-August, as the loss rate depends on the chlorine activation and hence, meteorology of the winters.

The very cold winter 2006 exhibits an extended period of loss rates of about 4 ppbvsh<sup>-1</sup> until early October, while the winter 2009 shows the shortest span of high loss rates, only until mid-August. The colder winter 2008 also exhibits high loss rates in most months, May–August in particular. In some winters (e.g. 2004 and 2008) the loss rates in August are also higher than those in September. The lidar measurements of Godin et al. (2001) in the Antarctic winters 1992–1998, and model studies of Tripathi et al. (2007) and Frieler et al. (2007) in the Antarctic winter 2003, also show comparable loss rates at 475 K. Our analyses are consistent with the loss rates found in the very cold Arctic winters (1994/1995,

1999/2000, 2004/2005, 2010/2011) during the peak loss rate period in January–February, for which loss rates of about 5–8 ppbvsh<sup>-1</sup> around 450–500 K are estimated (Kuttippurath et al., 2012, 2010; Frieler et al., 2007). No significant ozone production is found at this altitude level.

At 675 K, large interannual variability is found in the ozone loss rates from June to August, which are about 2–5 ppbvsh<sup>-1</sup>, depending on day of year and winter. The loss rates are typically about 2 ppbvsh<sup>-1</sup> in September and then increase rapidly to 4–6 ppbvsh<sup>-1</sup> thereafter. For instance: in 2005, the largest ozone loss rates of 3–5 ppbvsh<sup>-1</sup> are simulated in early winter, whereas about 3 ppbvsh<sup>-1</sup> is calculated in 2008. The lowest loss rates among the ten winters during the ozone hole period (June–September) are found in the warm winters of 2010 and 2012, about 1–2 ppbvsh<sup>-1</sup>. Note that a similar range of loss rates of 2–7 ppbvsh<sup>-1</sup> is also calculated for the colder Arctic winters in late March and mid-to late April in 2010/2011, February–March in 2008/2009 and March in 2004/2005, depending on day of year (Kuttippurath et al., 2010, 2012).

The production rates at 675 K show large variations from one year to the other, from zero in mid-August to 7 ppbvsh<sup>-1</sup> in late October. These substantial production rates in the September–October period offset the large loss rates during the same period. The high production rates at the end of winter are expected as small disturbances (toward the final warming) shift the polar vortices to sunlit parts of the mid-latitudes. The analyses on the ozone production and loss rates at 675 K imply that the ozone loss in the middle stratosphere also depends on the position of the polar vortex in sunlight and the dynamics of the winter.

#### 4 Conclusions

The interannual variability of the Antarctic winter meteorology was relatively large in the last decade (2004–2013), which included an extremely cold winter (2006), three moderately cold winters (2005, 2008, 2011), and three warm winters (2004, 2010, 2012). As analyzed from the average of the ten winter simulations, ozone loss in the Antarctic starts at the edge of the vortex at low EqLs (65–67° EqL) by mid-June, consistent with the findings of Lee et al. (2000). Ozone loss progresses with time and advances to higher EqLs (69–83° EqL), with the largest loss at lower EqLs (65–69° EqL) in June–August in agreement with the exposure of the vortex to sunlight. The maximum ozone loss is attained in the mid-September to mid-October period. The peak ozone loss (> 2 ppmv) is found over a broad altitude range of 475–550 K. The maximum modeled ozone loss is about 3.5 ppmv around 550 K in 2005 and 2006, the coldest winters with the largest loss. In contrast, the maximum loss in the warmer winters of 2004, 2010 and 2012 was restricted to 2.6 ppmv. The modeled column loss shows the largest value of 173 DU in 2005 and the lowest of 110 DU in 2004 over 350–850 K,

consistent with the meteorology of the winters. The comparison between simulated and observed trace gas evolution during the winters suggests that the diabatic descent during spring is slower in the model. Therefore, the amount of chlorine available to be activated in spring is lower in the model and hence, the simulated ClO is smaller than the measurements in the lower stratosphere below 550 K, leading to less simulated chemical ozone loss. However, the slower descent also leads to less ozone-rich air being brought down from above. Simulated ozone values reflect a balance between these two effects.

In the lower stratosphere at 500 K, the ozone loss rates have a comparable distribution in all winters, with about 2–3 ppbvsh<sup>-1</sup> in July and 4–5 ppbvsh<sup>-1</sup> from August to late-September. However, as expected, the very cold winters are characterized by slightly larger and extended periods of high loss rates. In the middle stratosphere at 675 K, a loss rate of about 2–5 ppbvsh<sup>-1</sup> in July–September, and a production rate of about 4–9 ppbvsh<sup>-1</sup> in September–October, are simulated. Therefore, these higher production rates largely outweigh the loss rates during the same period.

Our study finds large interannual variability in Antarctic ozone loss in the recent decade with a number of winters showing shallow ozone holes, but also with the year of the maximum ozone hole in the last decades. These smaller ozone holes or ozone losses are mainly related to the year to year changes in dynamical processes rather than the variations in anthropogenic ODSs, as the change in ODS levels during the study period was very small.

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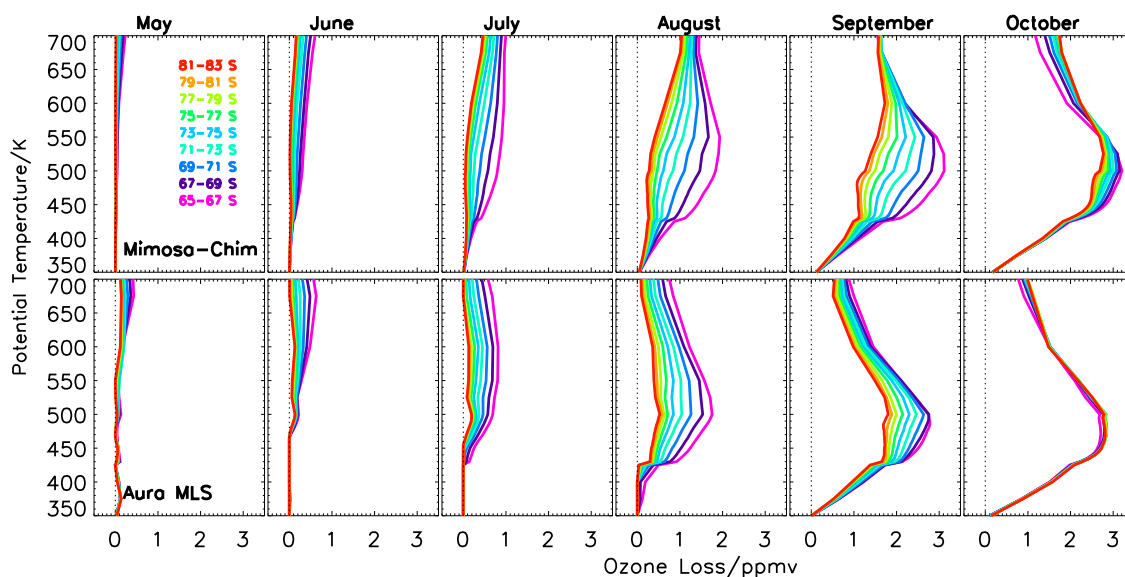
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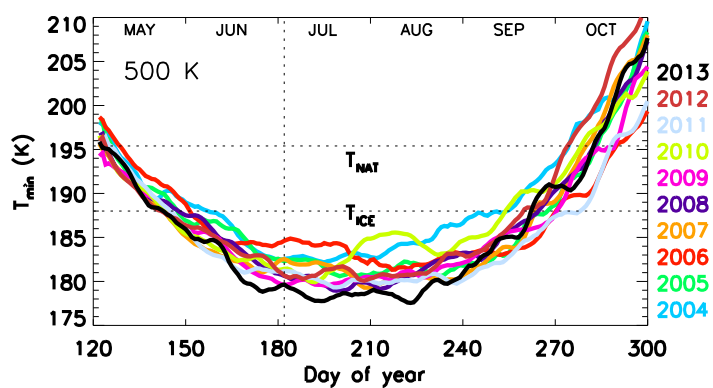
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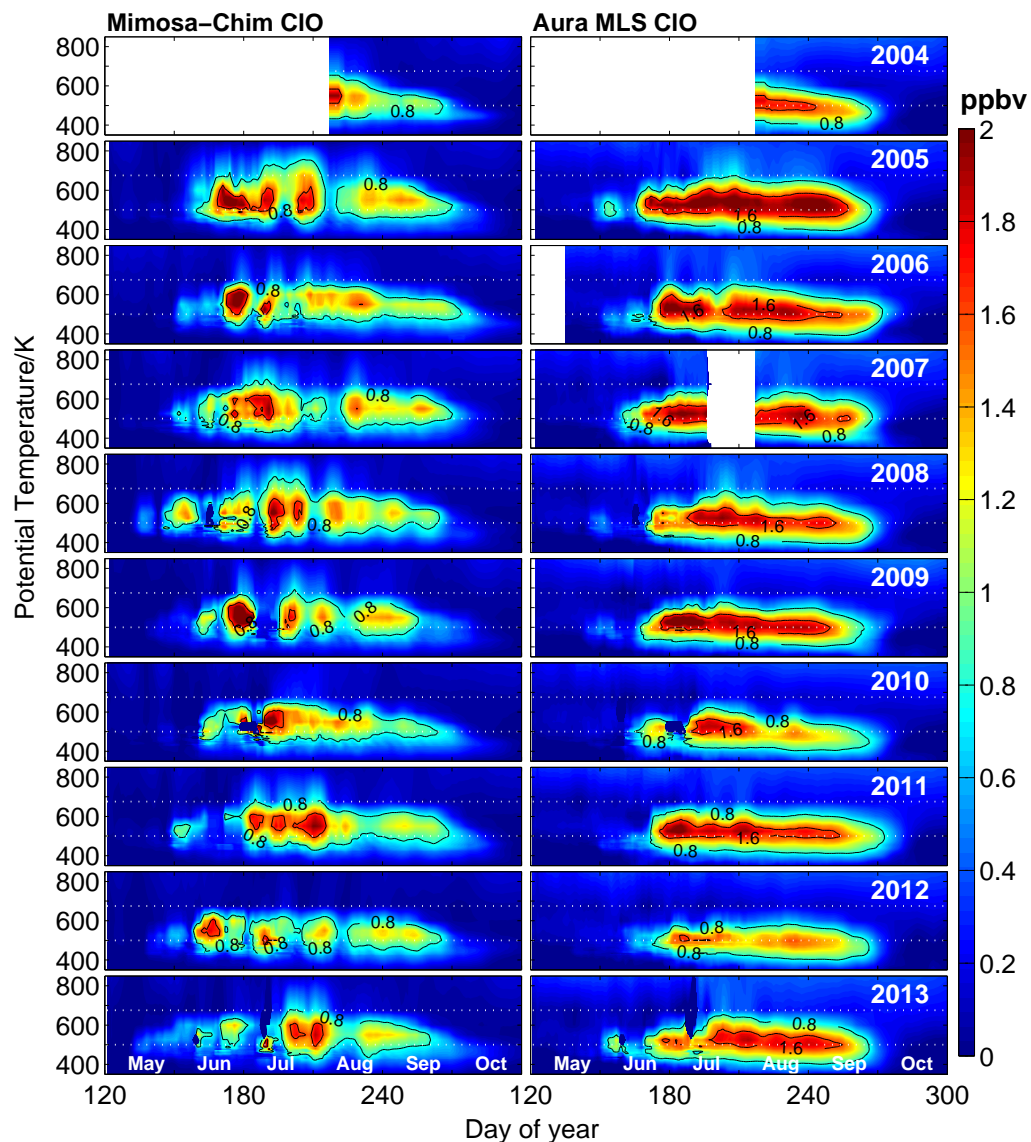


**Fig. 1.** The ten year (2004–2013) average monthly mean ozone loss estimated at different equivalent latitude (EqL) bins (of  $2^\circ$ ) from  $65$  to  $83^\circ$  S EqL from the Mimosa-Chim simulations and MLS measurements. The model results are interpolated with respect to the time and location of the MLS measurements inside the vortex and then averaged for the corresponding day. The Y-axis represents potential temperature in Kelvin (K). The black dotted lines represent  $0$  ppmv.

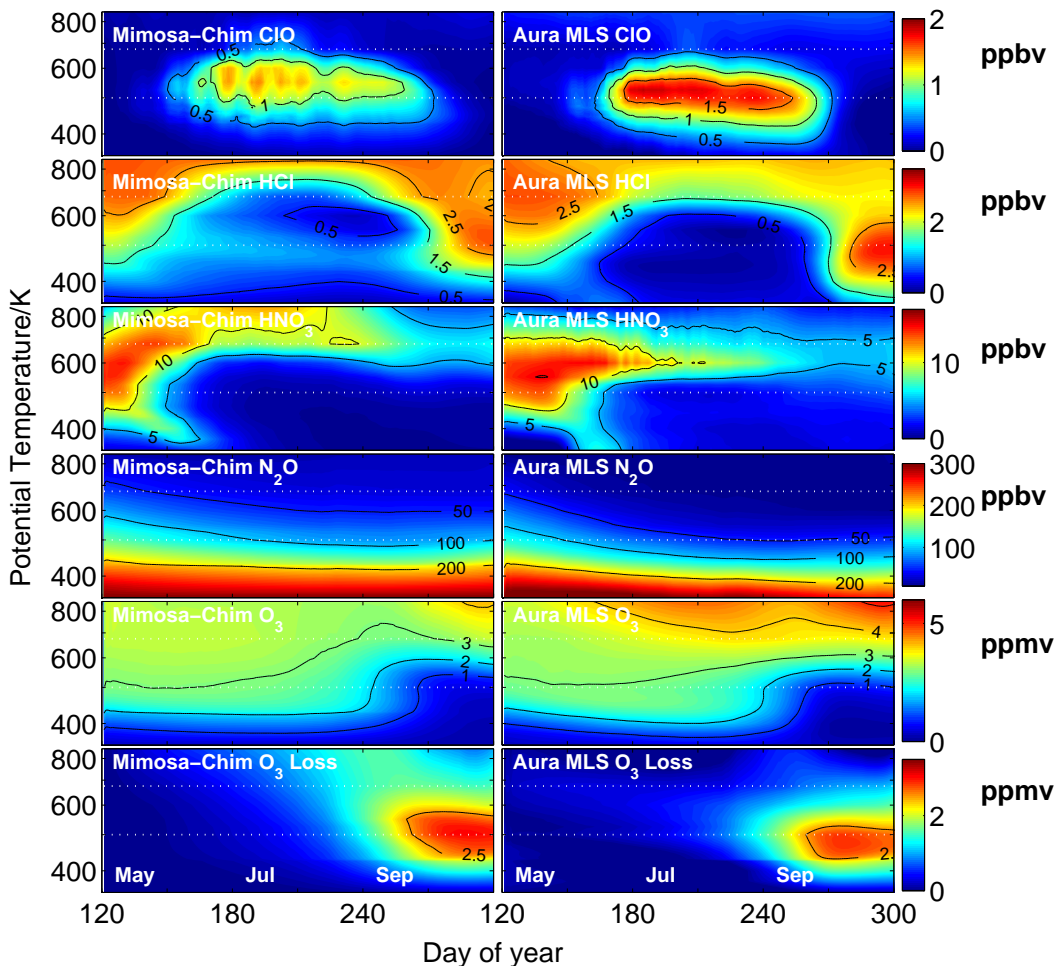


**Fig. 2.** Evolution of polar cap (50–90° S) minimum temperature derived from the ECMWF operational analyses for each winter from 2004 to 2013 at 500 K ( $\sim 19$  km) potential temperature. The  $T_{NAT}$  and  $T_{ICE}$  thresholds are also marked.

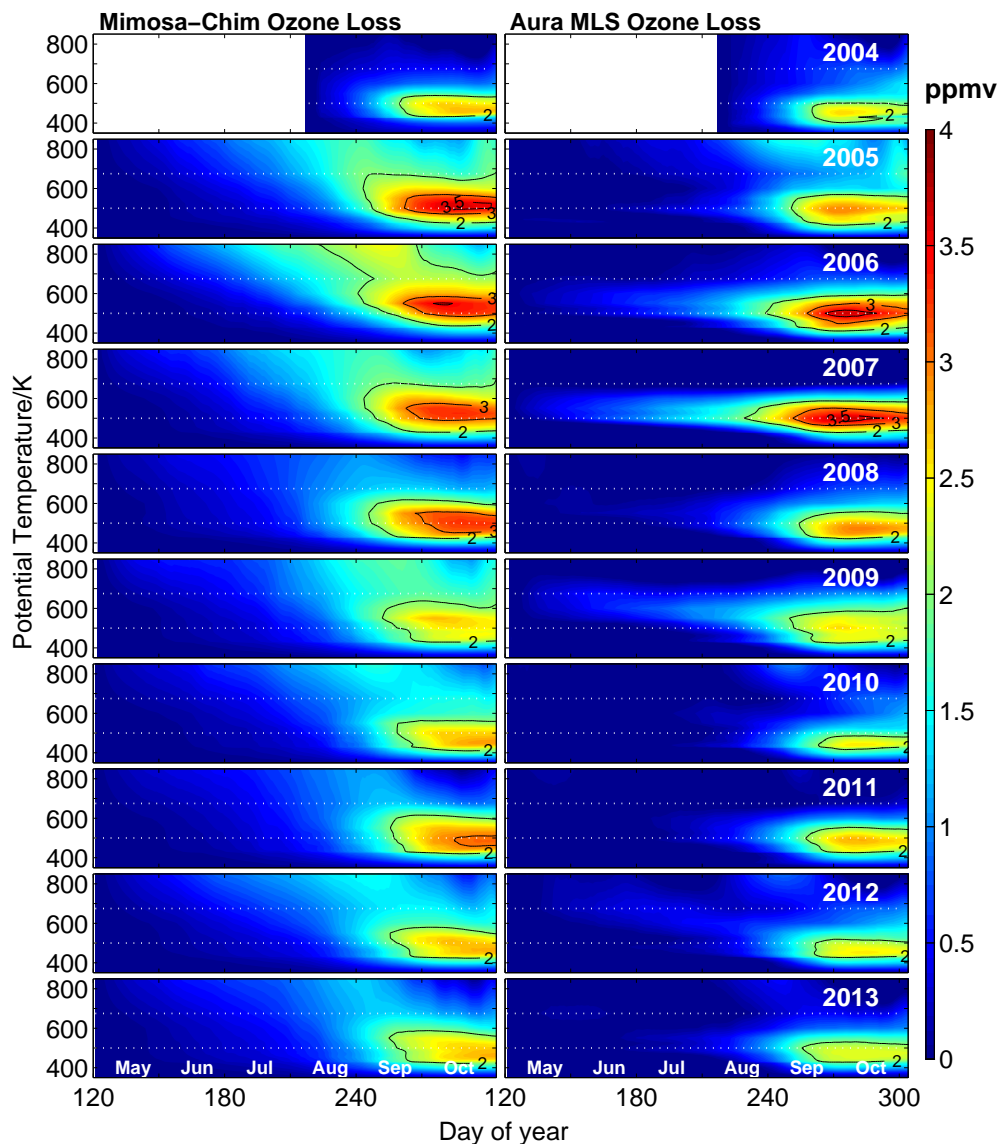




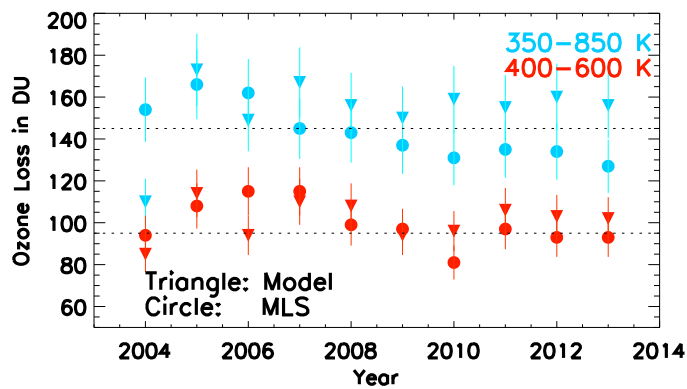
**Fig. 3.** Vertical distribution of the vortex averaged (defined by  $\geq 65^\circ$  EqL) ClO estimated from the Mimosa-Chim model and MLS measurements for the Antarctic winters 2004–2013. The model results are interpolated with respect to the time and location of the MLS measurements inside the vortex and then averaged for the corresponding day. ClO data are not available during early May 2006, and late July and early August 2007. The measurements are selected with respect to local solar time 10–16 h and solar zenith angles below  $89^\circ$  as available. Both model results and MLS data are smoothed for seven days. The Y-axis represents potential temperature in Kelvin (K). The white dotted lines represent 500 K ( $\sim 19$  km) and 675 K ( $\sim 26$  km).



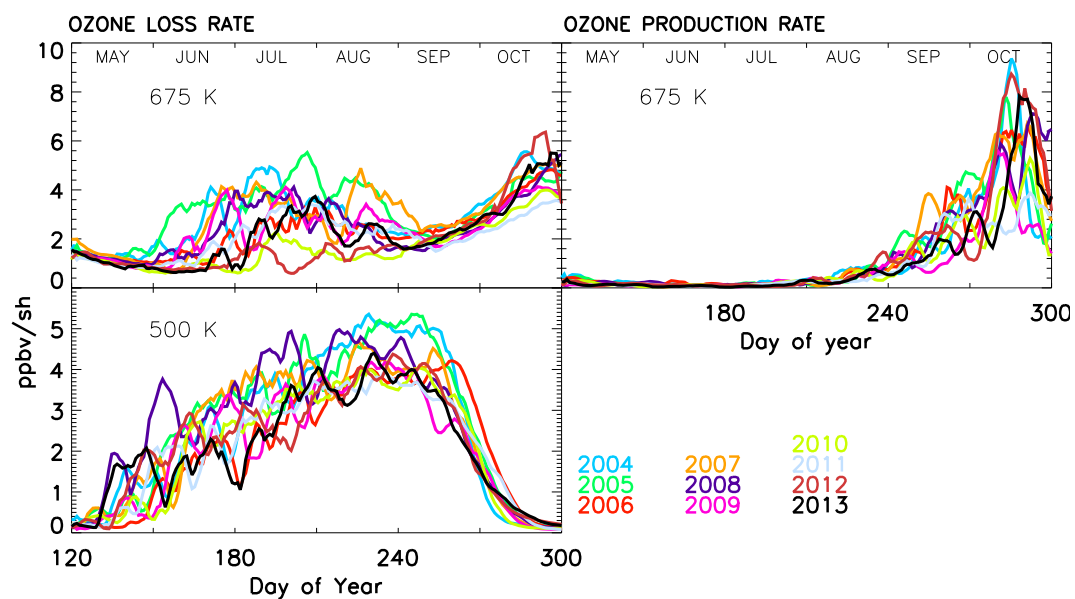
**Fig. 4.** The vortex averaged (defined by  $\geq 65^\circ$  EqL) vertical and temporal evolution of CIO, HCl, HNO<sub>3</sub>, N<sub>2</sub>O, O<sub>3</sub> and ozone loss from the Mimosa-Chim model and MLS measurements. The model results are interpolated with respect to the time and location of the MLS observations inside the vortex and then averaged for the corresponding time period. The data are the average of ten Antarctic winters in 2004–2013 and are smoothed for 7 days. CIO data are not available during early May 2006, and late July and early August 2007. The CIO measurements are selected with respect to local solar time 10–16 h and solar zenith angles below  $89^\circ$  as available. The Y-axis represents potential temperature in Kelvin (K) and is in logarithmic scale. The white dotted lines represent 500 K ( $\sim 19$  km) and 675 K ( $\sim 26$  km).



**Fig. 5.** Vertical distribution of the vortex averaged (defined by  $\geq 65^\circ$  EqL) ozone loss estimated for the Antarctic winters 2004–2013. The model results are interpolated with respect to the time and location of the MLS measurements inside the vortex and then averaged for the corresponding day. Left: the ozone loss derived from the difference between the passive ozone and the chemically integrated ozone by Mimosa-Chim. Right: the ozone loss derived from the difference between the Mimosa-Chim passive ozone and the ozone measured by MLS. Both model results and MLS data are smoothed for seven days. The Y-axis represents potential temperature in Kelvin (K). The white dotted lines represent 500 K ( $\sim 19$  km) and 675 K ( $\sim 26$  km).



**Fig. 6.** Vortex averaged (defined by  $\geq 65^\circ$  EqL) column ozone loss computed from model simulations and measurements, during the maximum ozone loss period in the Antarctic, at 350–850 K and 400–600 K for the 2004–2013 period. The estimated uncertainty of the column loss computed from both simulations and measurements is about 10 % (e.g. Kuttippurath et al., 2011).



**Fig. 7.** Vortex averaged (defined by  $\geq 65^\circ$  EqL) chemical ozone loss and production rates at 675 K ( $\sim 26$  km) and 500 K ( $\sim 19$  km) in ppbv per sunlit hour ( $\text{ppbv sh}^{-1}$ ) for the Antarctic winters 2004–2013 estimated from the Mimosa-Chim model simulations.