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Estimation of Arctic ozone loss in winter 2004/05 based on assimilation of EOS MLS and SBUV/2 observations

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ABSTRACT: In this paper we present a new technique for the estimation of ozone loss in the stratospheric polar vortex based on the assimilation of Earth Observing System Microwave Limb Sounder (EOS MLS) and Solar Backscatter Ultraviolet radiometer (SBUV/2) ozone observations in the Met Office data assimilation system. We focus on the northern winter of 2004/05, which was exceptionally cold in the Arctic stratosphere, with associated large ozone depletion due to heterogeneous chemistry. Our ozone loss estimate, which was calculated for the 1 February to 10 March 2005 period, peaks at 450 K (approximately 17–18 km), and is 0.6 ppmv at that isentropic level (our loss estimate for the vortex core only was somewhat higher (1.0 ppmv) and indicates uncertainties related to mixing at the vortex edge). This value is similar to or smaller than results from other studies, which estimate ozone loss in this period to be in the 0.6–1.2 ppmv range. When combined with results from other studies that estimate ozone loss occurring outside our assimilation period, we obtain an estimate of 0.8–1.2 ppmv for ozone loss from early January to early March 2005.
We find a second maximum in ozone loss for the 1 February–10 March period near 650 K (approximately 25 km) of around 0.4 ppmv. This is a lower figure than found in other studies, but ozone loss is actually much stronger at this level outside the vortex in a low-ozone pocket in the Aleutian anticyclone, likely due to the NOx catalytic cycle. Our results show that the ozone data assimilation method we have used to estimate ozone loss is very promising, and can lead to potentially more accurate ozone-loss estimates than other methods. © Royal Meteorological Society and Crown Copyright, 2008.

KEY WORDS polar ozone depletion; data assimilation; stratosphere

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1. Introduction

Arctic lower stratospheric temperatures were exceptionally cold during winter 2004/05. Large areas where the temperature dropped below the threshold temperature for Type I polar stratospheric cloud (PSC) formation, or T_{NAT} (where NAT is nitric acid trihydrate), were already found in early December and persisted into March, albeit decreasing dramatically after mid-February. Anomalously cold temperatures below T_{NAT} were also found in the lowermost stratosphere, at theta levels lower than 400 K (Feng *et al.*, 2007; Rex *et al.*, 2006). The period with temperatures below T_{NAT} at 50 hPa was the longest on record (Manney *et al.*, 2006), which meant that the winter-mean PSC volume was also the largest on record (Rex *et al.*, 2006). In late January, ODIN/SMR satellite observations revealed significant uptake of nitric acid over the Arctic and North Atlantic, an indication of PSC formation (Urban *et al.*, 2006). Low abundances of nitric acid at 20 km and slightly enhanced abundances at 15 km, inferred from airborne measurements inside the vortex in late January and early February, were in fact indicative of denitrification occurring (Kleinbohl *et al.*, 2005). Satellite measurements by Atmospheric Chemistry Explorer (ACE) (Jin *et al.*, 2006a) also indicated inhomogeneous denitrification in the vortex between mid-January and mid-March, between 400 K and 550 K.

The area where the more rare ice PSC Type II could form, at even colder temperatures, was also among the largest in the observational record at 50 hPa, along with the winters 1995/96 and 1983/84. On 26 January, Type II PSCs were in fact observed for the first time in 15 years of observations above Spitzbergen (79°N) (Maturilli and Dörnbrack, 2006). Associated with this, large-scale dehydration, where there is uptake of water out of the gas phase, presumably during ice cloud formation, was detected by EOS MLS over parts of the Arctic at 18–19 km at around the same time (Jimenez *et al.*, 2006). It should, however, be noted that, despite this dehydration event, the dehydration in the Arctic for the whole of the 2004/05 winter was not significant.

The presence of the PSCs leads to heterogeneous reactions, which activate chlorine and thus lead to ozone loss. Recent observational and modelling studies (eg Dufour *et al.*, 2006; Urban *et al.*, 2006; Santee *et al.*, 2008), which have focused on the northern winter of 2004/05 and other recent winters, have led to a better understanding of stratospheric chlorine partitioning and how both

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reactive and reservoir chlorine evolves through the polar winter. Previously, many aspects of stratospheric chlorine partitioning had remained uncertain, and the better understanding of this partitioning resulting from these recent papers is essential in better understanding ozone loss and predicting stratospheric ozone loss in the future.

The winter was also dynamically active. Marked, episodic intrusions of mid-latitude air into the lower stratospheric vortex occurred in late January, and even more frequently in February, as revealed by N_2O and H_2O EOS MLS observations (eg Manney *et al.*, 2006). A strong intrusion in late January was reminiscent of a similar event observed during the European Arctic Stratospheric Ozone Experiment (EASOE) campaign in January 1992 (Orsolini *et al.*, 1995), and led to a large in-mixing of mid-latitude tongues of air into the vortex. N_2O mixing ratios increased inside the polar vortex below 500 K, starting in late February, indicating that horizontal transport of mid-latitude N_2O-rich air into the vortex overwhelmed N_2O lowering due to descent (Manney *et al.*, 2006). Moreover, the descent maximized in the vortex edge region during perturbed dynamical conditions. Eventually, by mid-March, an early final warming led to a vortex split in the lower stratosphere, and the temperatures rose above T_{NAT}.

As a result of the potential for large ozone loss in the 2004/05 winter, many observational and model-based estimates of ozone loss have been published, and these are summarized in section 2. These estimates have been made using a variety of methods and the size of the calculated ozone loss varies, which indicates potential difficulties with the existing methods used. These difficulties are exacerbated in the 2004/05 winter because the more active mixing and the greater potential for ozone loss at low altitudes, where the vortex edge is less defined, renders the task of estimating ozone loss inside the polar vortex harder than in other years.

To address these issues, in this paper we estimate vortex ozone loss using a method based on the assimilation of Solar Backscatter Ultraviolet radiometer (SBUV/2) and EOS MLS ozone data by the Met Office data assimilation system. The ozone assimilation enables the calculation of local ozone loss over northern hemisphere mid and high latitudes. The aim of this approach is to better account for the effect of horizontal mixing and to preserve spatial ozone loss inhomogeneities in the polar vortex.

2. Summary of other ozone loss estimates for winter 2004/05

Various methods are used to estimate bulk, vortex-averaged ozone loss (see WMO, 2006 for more details), and they often crudely account for horizontal mixing across the vortex edge and inhomogeneous descent.

Ozone loss can be inferred from changes in the *compact correlations* between ozone and long-lived tracers between early and late winter. Inferred ozone loss can be affected by mixing across the vortex edge, as the correlation lines are different inside and outside the vortex. The *profile-descent* method relies on estimating vortex-averaged descent as an altitude shift derived from comparison of long-lived tracers in early and late winter. The altitude shift is then applied to an ozone profile from early winter, and the difference from an ozone profile measured in late winter is attributed to ozone loss. The *vortex-average method* instead relies on a radiative heating rate calculation to estimate the bulk descent in the vortex, and the alteration of an initial ozone profile. *The Lagrangian Match technique* uses multiple sampling of an air mass by in situ or satellite measurements to infer ozone loss along the assumed trajectory. For winter 2004/05, several variants of the above methods were applied by Jin *et al.* (2006b) using ACE data, Manney *et al.* (2006) using EOS MLS data, Rex *et al.* (2006) using Polar Ozone and Aerosol Measurement (POAM), Stratospheric Aerosol and Gas Experiment (SAGE) and sonde data, and von Hobe *et al.* (2006) using aircraft measurements.

The passive subtraction method compares observed ozone with a reference field which represents the evolution of ozone in the absence of chemical depletion. Typically, such an ozone field is initialized from climatology or observations, and passively transported through the winter in an off-line model. To separate the effect of ozone transport, the reference ozone is then subtracted from ozone observations. The reference ozone can also be pseudo-passive, with heterogeneous chemical reactions on PSCs switched off, but gas phase catalytic cycles still active. Such an approach becomes increasingly important at longer timescales (greater than around a month) and also at levels above around 650 K, where the impact of NO_x chemistry is greater. Singleton *et al.* (2005) compared results using passive and pseudo-passive approaches. Singleton *et al.* (2007) used a variety of satellite observations and transported passive ozone to infer the winter 2004/05 ozone loss.

Observation-based ozone loss estimates were compared in WMO (2006). In summary, at the 450 K level one finds, for the early January to early March period, a first cluster of conservative values around 1.2 ppmv (Manney *et al.*, 2006; Rex *et al.*, 2006), while values as high as 2.3 ppmv were found by Jin *et al.* (2006b) and Singleton *et al.* (2007). Ozone loss values were also higher in von Hobe *et al.* (2006), but were a local measure and not a vortex-average. Hence there is a wide of range of ozone loss estimates, with discrepancies nearly as large as a factor of two.

Most studies showed that the maximum relative ozone loss occurred at lower altitudes (e.g. 425–450 K) than in other years characterized by large ozone losses in the Arctic, such as winter 1999/2000. This led to the highest column ozone loss (up to 120 Dobson units (DU)) ever estimated for the Arctic, which falls on the high end of the compact, near-linear relationship between column ozone loss and PSC volume established for the last 15 winters (Rex *et al.*, 2006).

Estimates of ozone depletion for the winter of 2004/05 made using the SLIMCAT model (Feng *et al.*, 2007; Singleton *et al.*, 2007) indicate a vortex-averaged ozone

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loss of around 1.8–2.3 ppmv between early January and mid-March at 450 K. Grooss and Müller (2007) used the Lagrangian CLAMS model and found a somewhat smaller vortex-averaged ozone depletion of 1.4 ppmv at 475 K. They also reported a distinct upper-level depletion (above 550 K), amounting to approximately 1.2 ppmv over the January to early March period, which they attributed to the NOx catalytic cycle. There is also a hint of upper level depletion in Jin *et al.* (2006b), in the form of a weak second maximum at 700 K.

Finally, ozone loss estimation from assimilated ozone fields was independently pursued by Rösevall *et al.* (2007a, b), who assimilated Odin Sub-Millimetre Radiometer (SMR) or EOS MLS observations for winters 2004/05 and 2006/07 in a chemical transport model (CTM) driven by European Centre for Medium-Range Weather Forecasts (ECMWF) analyses. For the early January-early March 2005 period and at 450 K, they found a vortex-averaged winter ozone loss of around 0.9–1.3 ppmv using EOS MLS data, although another study made using Odin/SMR data gave an ozone loss estimate of 0.6–0.9 ppmv. Note that, unlike our approach, vertical motion was not represented explicitly but was estimated both from N_2O observations and diabatic cooling rates calculated by the SLIMCAT CTM, and a number of simulations were made, using a range of vertical transport rates.

3. Ozone loss estimation based on data assimilation

Here, we assimilate ozone satellite observations to calculate local ozone loss over the northern hemisphere mid and high latitudes, with the aim of better accounting for the effect of horizontal mixing and preserving spatial ozone loss inhomogeneities in the polar vortex. The assimilation scheme is based on a three-dimensional variational (3D-Var) version of the operational Met Office assimilation system (Lorenc *et al.*, 2002), and uses a forecast model that is semi-Lagrangian with a height-based vertical coordinate (Davies *et al.*, 2005). The model version used here has 50 levels from the surface to around 63 km and a horizontal resolution of 2.5° latitude × 3.75° longitude. EOS MLS and SBUV/2 ozone observations are assimilated, together with dynamical observations from satellites, aircraft, radiosondes and surface stations. The ozone assimilation scheme is described in Jackson and Saunders (2002) and Jackson (2004) and the impact of the assimilation of EOS MLS and SBUV/2 data on ozone analyses is described in Jackson (2007). Because the assimilation runs are computationally relatively expensive, they were limited to the 26 January–10 March period, rather than the entire winter. Thus the primary intention of this paper is to demonstrate that our technique is a feasible means of estimating ozone loss. Estimates of ozone loss for an entire winter using this technique can be attempted in subsequent studies.

Two sets of satellite observations were assimilated. The first are the near-global, daily ozone observations from EOS MLS. Version 1.51 retrievals between 215 and 0.46 hPa are used, with a vertical resolution of about 3 km in the stratosphere, and an along-track resolution of 165 km (when the experiments were performed, the newer Version 2.2 EOS MLS retrievals were not available). The ozone retrievals agree within 5–10% with correlative measurements (Froidevaux *et al.*, 2006). The temporal resolution of the observations is adequate to study ozone depletion, as, at a given location, the 'revisit time' is of the order of 1 day. The second set of ozone observations assimilated comprises layer-mean ozone amounts from SBUV/2. The data are available in 6 coarse vertical layers (1000–16, 16–8, 8–4, 4–2, 2–1 and 1–0.1 hPa). The horizontal resolution is about 200 km, and no observations are made in the polar night. Jackson (2007) showed that the SBUV/2 data have a small positive impact on the quality of the ozone analyses, but the positive impact seen when adding EOS MLS data is much greater.

In the assimilating model, ozone photochemistry is parametrized using a version of the Cariolle-type schemes (Cariolle and Deque, 1986), which have recently been re-evaluated by Geer *et al.* (2007). It is important to point out that no ozone heterogeneous chemistry is included. A realistic ozone field is established before the bulk ozone destruction occurs, and is produced by running the ozone assimilation for 6 days, starting 26 January and ending 1 February. Thereafter, the ozone assimilation run is continued through to 10 March and a reference run is also started using the same initial conditions on 1 February. The reference run is like the assimilation run, except that no ozone observations are assimilated and the Cariolle scheme is switched off. Because the ozone assimilation is univariate, and there is also no feedback between the analyzed ozone and the model radiation scheme, the dynamical fields in both runs are near-identical. Therefore, differences between the assimilated and reference ozone fields should not be caused by differences in transport between the runs and can thus be attributed to chemistry. In the middle- and high-latitude winter lower stratosphere, the ozone lifetime due to gas-phase reactions is very long, and so it is likely that these chemical changes will result overwhelmingly from heterogeneous PSC-related chemistry. The 6-day initialization step ensures that the reference ozone is realistic and shares the same potential observational biases as the assimilated ozone.

Model background errors determine the weight given to the observations relative to the model forecast. For ozone, the horizontal error correlations are isotropic and Gaussian, with a length-scale of 600 km, and the error standard deviation in the stratosphere is small – around 3% of climatological ozone values in the lower stratosphere, falling to around 1% near 10 hPa.

4. Assimilation-based ozone loss estimates

Here, we discuss the ozone and ozone loss evolution inside the vortex and in the extratropics. Vortex averages are based on the same scaled potential vorticity criterion as in Manney *et al.* (2006), i.e. scaled potential vorticity

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greater than or equal to 1.6×10^{-4} s^{-1} throughout the vortex, and greater than or equal to 2.2×10^{-4} s^{-1} in the vortex core. Figure 1(a) shows the time evolution of vortex-averaged ozone loss, i.e. differences between ozone from the assimilation and reference runs, on seven isentropic levels between 400 and 700 K. The largest ozone loss is seen at 450 and 650 K, and the only level where ozone increases is 550 K. At the lower levels (below 550 K) the ozone loss is nearly monotonic with time, indicating the steady impact of chemical ozone loss throughout the experimental period. However, between 600 and 700 K some large daily fluctuations between ozone loss and ozone gain are seen, especially between 16 and 20 February. These changes are discussed in more detail later in this section.

Figure 1(b) shows the time-evolution of the EOS MLS observations and the assimilated ozone (sampled like EOS MLS) on the 450 K and 650 K levels, averaged over the vortex. The analyses overestimate ozone, compared with EOS MLS. This is possibly due to the absence of ozone-destroying heterogeneous chemistry in the forecast model, and may indicate that the ozone background error covariance used is too small, as shown by Jackson (2004). However, the rate of ozone loss during the experimental period is similar to that observed by EOS MLS. In addition, because the ozone loss shown in Figure 1(a) is the difference between assimilated and reference ozone, the high bias seen in Figure 1(b) should be eliminated in the ozone loss estimation.

Figure 2 shows the vortex-averaged ozone loss profile. Here, the ozone loss is calculated by taking the difference between the ozone loss values shown in Figure 1(a) at the end of the run on 10 March and at the start of the run on 1 February. Figure 2 shows that the mean ozone loss at 450 K is 0.6 ppmv and at 650 K is 0.4 ppmv.

We find peak ozone depletion near 450 K as in other studies (Manney *et al.*, 2006; Rex *et al.*, 2006; Singleton *et al.*, 2007). The magnitude of the loss, nearly 0.6 ppmv, is smaller than many other estimates: for the 1 February–10 March period, Grooss and Müller

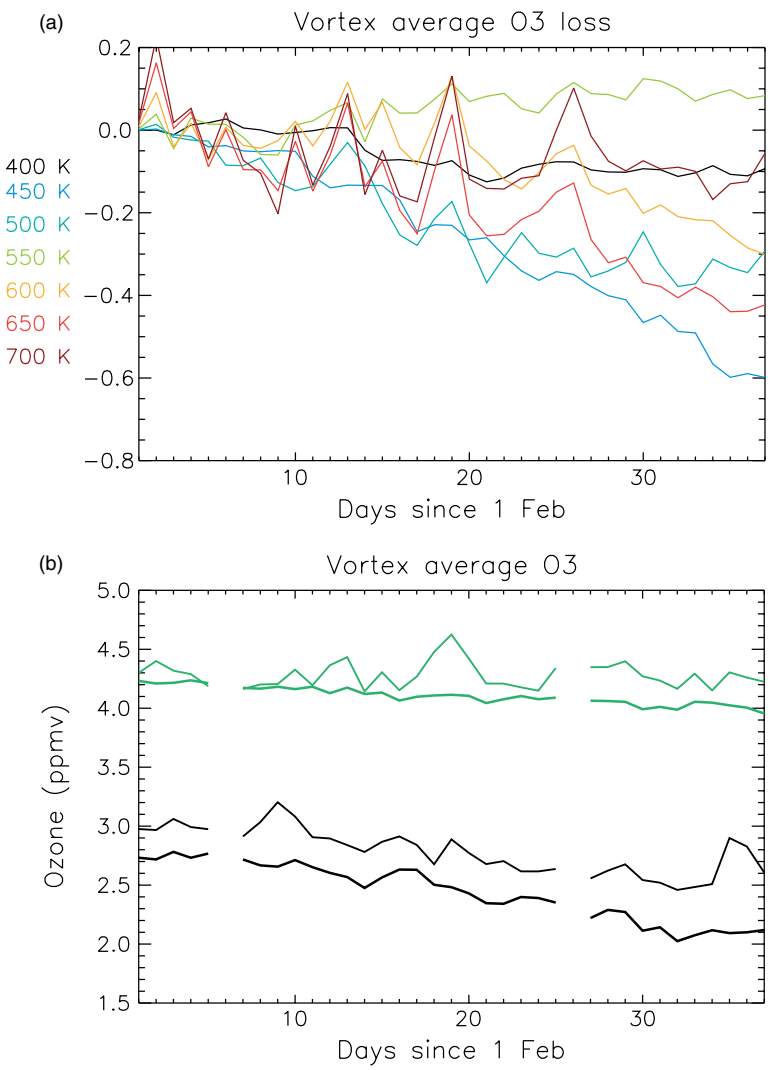

Figure 1. (a) Vortex average ozone loss for selected isentropic levels from 400 to 700 K (the levels are indicated by the colour key). The *y*-axis shows ozone loss in ppmv, the *x*-axis shows days from 1 February 2005. Negative values indicate ozone loss. (b) Vortex average ozone for the assimilation run (thin lines) and from EOS MLS observations (thick lines) for the 450 K (black) and 650 K (green) isentropic levels. Units are ppmv.

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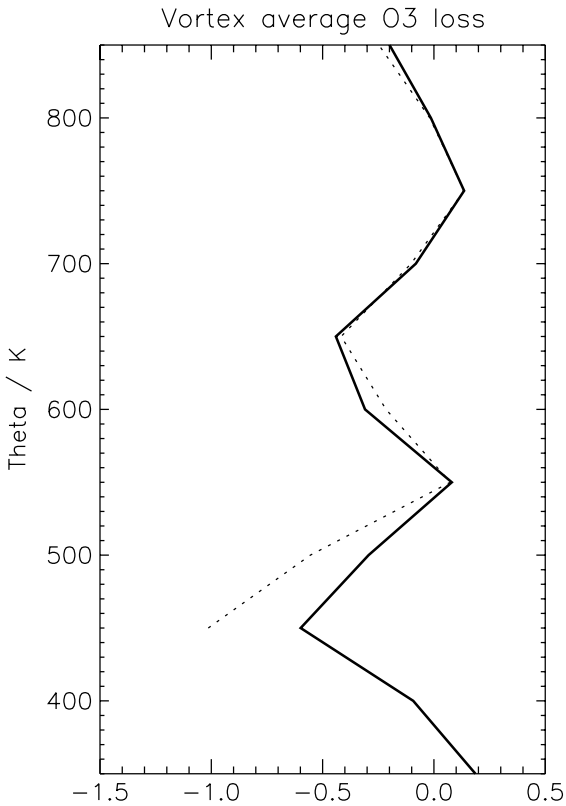

Figure 2. Average ozone loss profile for whole vortex (solid) and vortex core (dashed). Negative values indicate ozone loss. Units are ppmv.

(2007) show an ozone loss of approximately 0.8 ppmv and Singleton *et al.* (2007) a loss of around 1.2 ppmv. Interestingly, our results agree best with those of Rösevall *et al.* (2008), who use an ozone loss estimation technique that is most similar to our own method (although they use a CTM and do not calculate vertical motion explicitly). Rösevall *et al.* (2007) estimate the ozone loss in the 1 February–10 March period to be in the 0.6–0.9 ppmv range, irrespective of whether it is calculated using Odin SMR or EOS MLS data.

Most other studies, apart from the three listed in the above paragraph, present ozone loss for the entire 2004/05 winter, and therefore we cannot directly compare our results with results from these studies. However, we can effect a rough comparison by utilizing the fact that Grooss and Müller (2007), Rösevall *et al.* (2008) and Singleton *et al.* (2007) all show that significant ozone depletion occurred during January, before the start of our experimental period: 0.6 ppmv according to Singleton *et al.* (2007), 0.3 ppmv according to Grooss and Müller (2007) and up to 0.2 ppmv according to Rösevall *et al.* (2008). Moreover, as indicated by Singleton *et al.* (2007), ozone loss continues only weakly after 10 March. Hence, if we combine our results from 1st February–10 March with the ozone loss estimates for January provided by these three other studies we arrive at an overall ozone loss estimate for the early January to early March period of 0.8–1.2 ppmv at 450 K. This number is in fair agreement with the conservative cluster of values (around 1.2 ppmv) reported by WMO (2006), and close to the 1.4 ppmv model estimate from Grooss and Müller (2007), but significantly lower than the loss of 1.8–2 ppmv or higher in other studies (Jin *et al.*, 2006b; von Hobe *et al.*, 2006; Feng *et al.*, 2007; Singleton *et al.*, 2007).

Figures 3 and 4 show maps of ozone loss at the 450 K and 650 K levels, respectively, on selected days during the assimilation experiment. Figure 3 shows that the ozone loss at 450 K is initiated in the periphery of the vortex core, and becomes progressively more homogeneous in the vortex. Positive values at the vortex edge at 450 K are due to the fact that the collar of high ozone that is present around the vortex edge is better represented in the assimilation run than in the reference run. Transport errors in the dynamical fields in both the assimilation and reference runs act to smear out the high-ozone collar, but the assimilation of the EOS MLS data tends to mask such errors in the assimilation run (as also reported by Jackson, 2007). (Of course, by the same argument the ozone loss seen near the vortex edge in Figure 3 need not necessarily be entirely due to chemistry, but can be affected by transport errors, too). Such differences between the assimilation and reference runs are also seen in Figure 5, which shows ozone fields from the two runs at 450 K on 10 February 2005. The assimilation run shows high ozone values near the vortex edge and lower values in the vortex core. The reference run has higher values within the vortex, indicating the absence of heterogenous ozone loss in this run, but the high-ozone collar is smeared out and the gradient on the equatorward side of the collar is usually much weaker than in the assimilation run.

The progression of ozone loss throughout the period of the experiment means that collar of high ozone is seen more outside than inside the vortex edge by the end of the run. Thus, Figure 3 indicates that ozone gain (due to smearing of the high-ozone collar) is seen between the 1.6×10^{-4} s^{-1} and 2.2×10^{-4} s^{-1} contours on 10 February 2005, but increasingly equatorward of the 1.6×10^{-4} s^{-1} contour at later dates.

The impact of the smearing of the high-ozone collar on ozone loss estimates is shown in Figure 2, where the ozone loss has been recalculated using an average over the vortex core only (as defined by Manney *et al.*, 2006). Above the 550-K level, the ozone loss estimate is hardly affected, but at 450 K the ozone loss estimate for the vortex core is around 0.4 ppmv higher than when an average over the whole vortex (vortex edge plus vortex core, as defined by Manney *et al.*, 2006) is used. This indicates the potential errors associated with estimating ozone loss in the lower stratosphere, where mixing across the vortex edge is important. These types of errors will presumably also be important in other studies (Manney *et al.*, 2006; Rösevall *et al.*, 2007, 2008) where ozone loss is calculated over the whole vortex rather than the vortex core.

We also find another maximum ozone loss near 650 K, as in Grooss and Müller (2007), but our estimate for 1 February to 10 March is 0.4 ppmv, which is clearly smaller than their value (around 0.6 ppmv for the 1 February to 10 March period).

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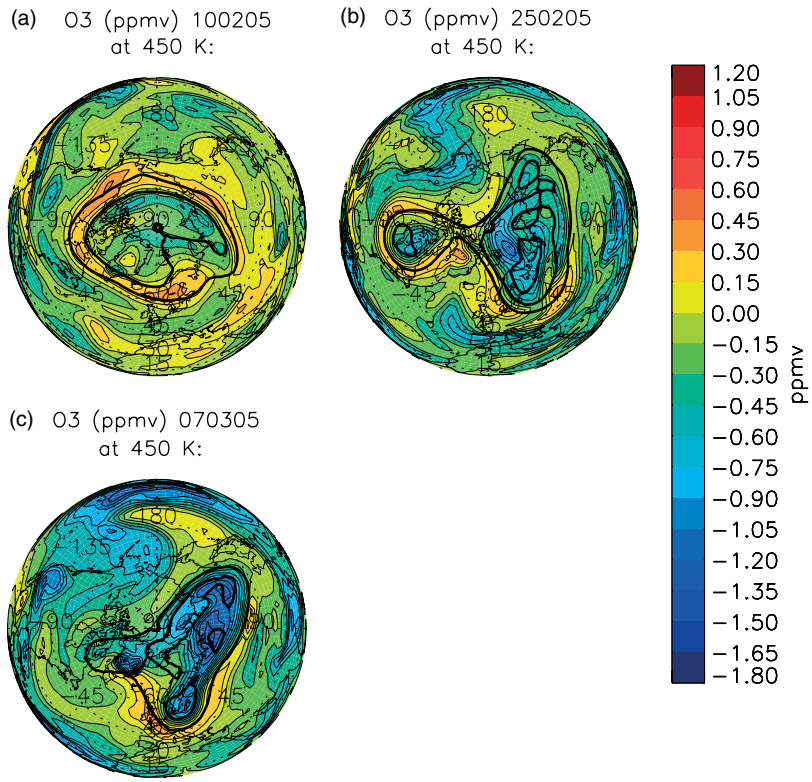

Figure 3. Ozone loss for the 450 K isentropic surface for (a) 10 February 2005, (b) 25 February 2005 and (c) 7 March 2005. Negative values indicate ozone loss. Units are ppmv. The outer (inner) bold solid line indicates a scaled potential vorticity value of 1.6×10^{-4} s^{-1} (2.2×10^{-4} s^{-1}), which indicates the criterion used for the edge of the whole vortex (edge of the vortex core).

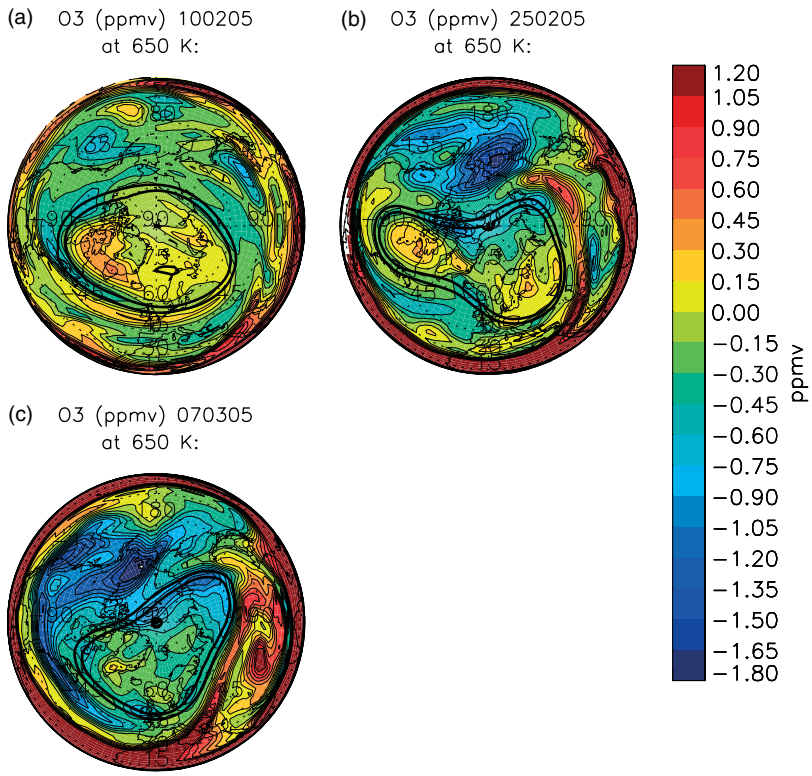

Figure 4. As Figure 3, except that ozone loss on the 650 K isentropic level is shown.

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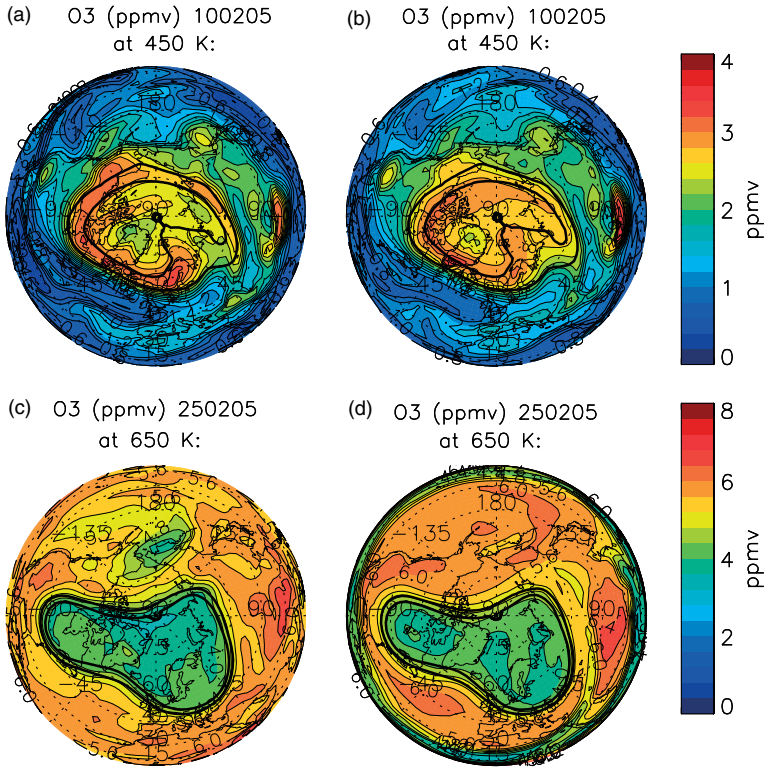

Figure 5. Ozone for 10 February 2005 at 450 K for (a) the assimilation run and (b) the reference run. Ozone for 25 February 2005 at 650 K for (c) the assimilation run and (d) the reference run. Units are ppmv.

However, the upper-level depletion is actually much stronger outside the vortex in the Aleutian anticyclone, where ozone is lower than the ambient value. This is also indicated by Figure 5, which shows low ozone in this location in the assimilation run at 650 K on 25 February, but not for the corresponding location in the reference run. Such a feature is likely to be a 'low-ozone pocket' (Harvey *et al.*, 2004). Examination of daily ozone maps shows that ozone-rich air is pulled out of the tropics within an anticyclone. A low ozone 'pocket' becomes evident around 7–8 February and deepens further over the next 2 weeks. The ozone depletion is assumed to be due to chemistry, and occurs rapidly, as evidenced by the ozone loss maps (Figure 4), with losses as large as 2 ppmv over the 1 February–10 March period. Such low-ozone pockets, especially in the Aleutian anticyclone, are recurrent features of the winter ozone distribution (Harvey *et al.*, 2004; Manney *et al.*, 1995). The ozone depletion is likely driven by the NOx catalytic cycle (Konopka *et al.*, 2007), and is rapid during the final warming. It also extends to lower levels in this case than those indicated in the low-ozone pocket climatology by Harvey *et al.* (2004), but is of the right order of magnitude.

Figure 1(a) shows some large daily fluctuations in ozone loss/gain between 600 and 700 K, especially between 16 and 20 February. These fluctuations are hard to attribute to chemical changes. A plot similar to Figure 1(b), but focusing on 700–850 K, also shows increases in EOS MLS ozone which are matched, or just followed by, larger increases in the assimilated ozone. Polar stereographic plots indicate that these fluctuations take place within the vortex core, not at the edge. It is not clear whether the fluctuations seen in the EOS MLS data are real or due to observation error. We speculate that the assimilation system is overestimating these increases for some reason and also spreading them downwards to reach 650 and even 600 K. This is reasonable since both the ozone background error correlation and variance increase with height through the lower stratosphere, so enabling the influence of the fluctuations at 700–850 K to be spread to lower levels. The response of the assimilation system is interesting and merits further investigation.

5. Summary and Discussion

In this paper we have presented a technique for estimating ozone loss in the stratospheric polar vortex based on the assimilation of EOS MLS and SBUV/2 observations. The technique has many similarities to the work presented by Rösevall *et al.* (2007a, b), although our approach has the advantage that vertical motion is represented explicitly by our assimilation system. Our vortex-averaged ozone loss estimate peaks at 450 K, in agreement with other studies, and is 0.6 ppmv for the 1 February–10 March period. When combined with estimates of January ozone from other studies, the loss magnitude of 0.8–1.2 ppmv for the early January to early March period is in fair agreement with many other estimates of ozone loss (WMO, 2006) made for this winter. We find a second maximum in the ozone loss vortex-averaged profile near 650 K, as shown by Grooss and Müller (2007), who attributed it to the NOx catalytic cycle. Our estimate (again, for the 1 February–10 March

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period) is lower than theirs in the vortex, but is much higher outside the vortex, in the low-ozone pocket formed by the Aleutian anticyclone. This result shows that an advantage of our technique is that it can identify ozone loss both inside and outside the polar vortex.

There are several factors arising from either the data itself, or the methodology, that could cause errors in inferred ozone loss. CTMs can produce diverging ozone-loss estimates due to the specific treatment of stratospheric chemistry or transport. The representativeness of sparse solar occultation measurements or in situ soundings for vortex-averaged quantities, even if supported by potential vorticity criteria, may account for some discrepancies. Indeed, ozone is quite inhomogeneous inside the vortex in early winter 2004/05. Hence, ozone values vary greatly in early winter inside the vortex, despite being at the same equivalent latitude. Transport of low-ozone extra-vortex air into the vortex at low levels could also contribute to the inaccuracy of profile descent methods.

Further evidence for transport errors in stratospheric analyses comes from Monge-Sanz *et al.* (2007), who performed age of air experiments in which the SLIMCAT CTM was driven by various analyses from ECMWF and the Met Office. They showed that stratospheric air was far younger in these experiments than observed. These results suggest that CTM-based estimates of ozone loss presented in other studies will also be affected by the quality of stratospheric analyses used.

Furthermore, estimation based on model reference ozone can lead to uncertainties if the ozone is not properly initialized, or if biases in satellite and reference ozone fields are not properly accounted for. As an example, we note that if we had chosen to estimate ozone loss by looking at the difference between EOS MLS observations and our reference run (instead of the difference between the assimilation and reference runs) then our ozone loss estimate at 450 K would be around 1.2 ppmv rather than 0.6 ppmv. The larger loss estimate is very similar to that found by Singleton *et al.* (2007), who also looked at differences between EOS MLS data and a model reference run. It is possible that the larger figure could arise from a lack of self-consistency in the reference and EOS MLS ozone (different biases, different transport), whereas in our approach we assume that many biases in the analysis are present in both assimilation and reference runs, and hence are eliminated when a difference between these runs is taken. This may be an explanation for the discrepancy between our results and those of Singleton *et al.* (2007) and others.

As already indicated, the above-mentioned problems can be avoided, or at least mitigated, by the approach we have used here to estimate ozone loss. However, the ozone assimilation has limitations of its own. Model background errors govern the weight given to the model background compared with the observations. Jackson (2004) showed that an increase in the current background error standard deviations can lead to reductions in stratospheric ozone analysis errors. It is hence possible that the smallness of the covariances means that the analyses here are too strongly weighted towards the background, and this may account for the overestimation of vortex ozone seen in Figure 1(b).

Another potential source of error worth discussing is the interplay between model transport errors and the ozone transport implicit in the assimilated ozone data. Jackson (2007) showed that the assimilation of EOS MLS ozone observations can counteract many of the ozone assimilation errors related to inaccurate model transport. It appears that throughout most of the stratosphere the transport from the analyzed wind fields and that implied by the EOS MLS data is similar, and so our results are not greatly affected by errors in model transport. However, an exception is the lower stratosphere, where there could be problems in interpreting our results. This is illustrated by Figures 3 and 5, where the transport implicit in the analyzed wind fields leads to a smearing of the high-ozone vortex 'collar' in the reference run, but the assimilation of EOS MLS data leads to a removal of this smearing in the assimilation run. Hence, there appears to be ozone gain in this 'collar' region (Figure 3) and the impact of this is that our estimate of ozone loss at 450 K can range from 0.6 to 1.0 ppmv, depending on whether we average over the whole vortex or simply the vortex core (see Figure 2). This suggests that further study is needed to reduce this potential source of error. There is also evidence that transport errors in stratospheric analyses may be reduced if using 4D-Var instead of 3D-Var assimilation (eg Monge-Sanz *et al.*, 2007). There is thus scope to reduce the errors in our ozone loss estimates by using 4D-Var instead of 3D-Var analyses. A 4D-Var ozone assimilation system is under development at the Met Office.

Confronting ozone analyses with observations in the way we have described in this paper can also minimize any errors in the representation of ozone chemistry. CTMs use accurate, comprehensive chemistry schemes but such schemes are not immune to errors. For example there are uncertainties in specifying the ClO dimer photolysis frequency (Pope *et al.*, 2007), which is important in determining ozone loss via the ClO dimer catalytic cycle (although, as pointed out by von Hobe *et al.* (2007), further laboratory and field studies are needed to confirm the results of the Pope *et al.* study). However, it should be stressed that simplified chemistry schemes, such as the Cariolle ozone chemistry scheme used here, although computationally very efficient, only represent gas-phase chemistry and are not effective substitutes for CTM chemistry schemes.

In conclusion, the technique we have used to estimate ozone loss is very promising. Because the technique is computationally relatively expensive, we restricted our study to the February–early March period, in order to demonstrate the feasibility and effectiveness of our method. This having being done, future studies should be focused on an entire winter. These future studies will also benefit from the fact that the ozone assimilation is part of an assimilation system that is constantly evolving and where the better description of model and observation errors is an ongoing requirement.

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References

Cariolle D, Deque M. 1986. Southern-hemisphere medium scale waves and total ozone disturbances in a spectral general circulation model. *J. Geophys. Res.* **921**: 10825–10846.

Davies T, Cullen MJP, Malcolm AJ, Mawson MH, Staniforth A, White AA, Wood N. 2005. A new dynamical core for the Met Office's global and regional modelling of the atmosphere. *Q. J. R. Meteorol. Soc.* **131**: 1759–1782.

Dufour G, Nassar R, Boone CD, Skelton R, Walker KA, Bernath PF, Rinsland CP, Semeniuk K, Jin JJ, McConnell JC, Manney GL. 2006. Partitioning between the inorganic chlorine HCl and $ClONO_2$ during the Arctic winter 2005 from the ACE-FTS. *Atmos. Chem. Phys.* **6**: 2355–2366.

Feng W, Chipperfield MP, Davies S, von der Gathen P, Kyrö E, Volk CM, Ulanovsky A, Belyaev G. 2007. Large chemical ozone loss in 2004/05 Arctic winter/spring. *Geophys. Res. Lett.* **34**: L09803, DOI: 10.1029/2006GL029098.

Froidevaux L, Livesey NJ, Read WG, Jiang YB, Jimenez CJ, Filipiak MJ, Schwartz MJ, Santee ML, Pumphrey HC, Jiang JH, Wu DL, Manney GL, Drouin BJ, Waters JW, Fetzer EJ, Bernath PF, Boone CD, Walker KA, Jucks KW, Toon GC, Margitan JJ, Sen B, Webster CR, Christensen LE, Elkins JW, Atlas E, Lueb RA, Hendershot R. 2006. Early validation analyses of atmospheric profiles from EOS MLS on the Aura satellite. *IEEE Trans. Geosci. Remote Sensing* **44**: 1106–1121.

Geer AJ, Lahoz WA, Jackson DR, Cariolle D, McCormack JP. 2007. Evaluation of linear ozone photochemistry parametrizations in a stratosphere–troposphere data assimilation system. *Atmos. Chem. Phys.* **7**: 939–959.

Grooss JU, Müller R. 2007. Simulation of ozone loss in Arctic winter 2004/05. *Geophys.Res. Lett.* **34**: L05804, DOI: 10.1029/2006GL028901.

Harvey VL, Pierce RB, Hitchman MH, Randall CE, Fairlie TD. 2004. On the distribution of ozone in stratospheric anticyclones. *J. Geophys. Res.* **109**: D24308, DOI: 1029/2004JD004992.

Jackson DR. 2004. Improvements in Ozone Data Assimilation at the Met Office. *Met Office NWP Technical Report No. 454*. Met Office: Exeter, UK.

Jackson DR. 2007. Assimilation of EOS MLS ozone observations in the Met Office data assimilation system. *Q. J. R. Meteorol. Soc.* **133**: 1771–1788.

Jackson DR, Saunders R. 2002. Ozone data assimilation: preliminary system. *Met Office Forecasting Research Technical Report 394*. Met Office: Exeter, UK.

Jimenez C, Pumphrey HC, MacKenzie IA, Manney GL, Santee ML, Schwartz MJ, Harwood RS, Waters JW. 2006. EOS MLS observations of dehydration in the 2004–2005 polar winters. *Geophys. Res. Lett.* **33**: L16806, DOI: 10.1029/2006GL025926.

Jin JJ, Semeniuk K, Manney GL, Jonsson AI, Beagley SR, McConnell JC, Rinsland CP, Boone CD, Walker KA, Bernath PF. 2006a. Denitrification in the Arctic winter 2004/2005: Observations from ACE-FTS. *Geophys. Res. Lett.* **33**: L19814, DOI: 10.1029/2006GL027687.

Jin JJ, Semeniuk K, Manney GL, Jonsson AI, Beagley SR, McConnell JC, Dufour G, Nassar R, Boone CD, Walker KA, Bernath PF, Rinsland CP. 2006b. Severe Arctic ozone loss in the winter 2004/05: observations from ACE-FTS. *Geophys. Res. Lett.* **33**: L15801, DOI: 10.1029/2006GL026752.

Kleinböhl A, Bremer H, Küllmann H, Kuttippurath J, Browell EV, Canty T, Salawitch RJ, Toon GC, Notholt J. 2005. Denitrification in the Arctic mid-winter 2004/2005 observed by airborne submillimeter radiometry. *Geophys. Res. Lett.* **32**: L19814, DOI: 10.1029/2006GL027687.

Konopka P, Engel A, Funke B, Müller R, Grooss J-U, Günther G, Wetter T, Stiller G, von Clarmann T, Glatthor N, Oelhaf H, Wetzel G, López-Puertas M, Pirre M, Huret N, Riese M. 2007. Ozone loss driven by nitrogen oxides and triggered by stratospheric warmings can outweigh the effect of halogens. *J. Geophys. Res.* **112**: D05105, DOI: 1029/2006JD007064.

Lorenc AC, Ballard SP, Bell RS, Ingleby NB, Andrews PLF, Barker DM, Bray JR, Clayton AM, Dalby T, Li D, Payne TJ, Saunders FW. 2002. The Met. Office global three-dimensional data assimilation scheme. *Q. J. R. Meteorol. Soc.* **126**: 2991–3012.

Manney GL, Froidevaux L, Waters J, Zurek R, Gille J, Kumer J, Mergenthaler J, Roche A, O'Neill A, Swinbank R. 1995. Formation of low-ozone pockets in the middle stratospheric anticyclone during winter. *J. Geophys. Res.* **100**: 13939–13950.

Manney GL, Santee ML, Froidevaux L, Hoppel K, Livesey NJ, Waters JW. 2006. EOS MLS observations of ozone loss in the 2004-2005 Arctic Winter. *Geophys. Res. Lett.* **33**: L04802, DOI: 10.1029/2005GL024494.

Maturilli M, Dörnbrack A. 2006. Polar stratospheric ice cloud above Spitsbergen. *J. Geophys. Res.* **111**: D18210, DOI: 10.1029/2005JD006967.

Monge-Sanz BM, Chipperfield MP, Simmons AJ, Uppala SM. 2007. Mean age of air and transport in a CTM: Comparison of different ECMWF analyses. *Geophys. Res. Lett.* **34**: L04801, DOI: 10.1029/2006GL028515.

Orsolini Y, Cariolle D, Déqué M. 1995. Ridge formation in the lower stratosphere and its influence on ozone transport: a GCM study during late January 1992. *J. Geophys. Res.* **100**: 11113–11135.

Pope FD, Hansen JC, Bayes KD, Friedl RR, Sander SP. 2007. Ultraviolet absorption spectrum of chlorine peroxide, CLOOCl. *J. Phys. Chem. A* **111**(20): 4322–4332.

Rex M, Salawitch RJ, Deckelmann H, von der Gathen P, Harris NRP, Chipperfield MP, Naujokat B, Reimer E, Allaart M, Andersen SB, Bevilacqua R, Braathen GO, Claude H, Davies J, De Backer H, Dier H, Dorokhov V, Fast H, Gerding M, Godin-Beekmann S, Hoppel K, Johnson B, Kyrö E, Litynska Z, Moore D, Nakane H, Parrondo MC, Risley Jr. AD, Skrivankova P, Stübi R, Viatte P, Yushkov V, Zerefos C. 2006. Arctic winter 2005: Implications for stratospheric ozone loss and climate change. *Geophys. Res. Lett.* **33**: L23808, DOI: 10.1029/2006GL026731.

Rösevall JD, Murtagh DP, Urban J, Feng W, Eriksson P, Brohede S. 2008. A study of ozone depletion in the 2004/05 Arctic winter based on data from ODIN/SMR and EOS/MLS. *J. Geophys. Res.* **113**: D13301. DOI: 10.1029/2007JD009560.

Rösevall JD, Murtagh DP, Urban J. 2007. Ozone depletion in the 2006/07 Arctic winter. *Geophys. Res. Lett.* **34**: L21809, DOI: 10.1029/2007GL030620.

Santee ML, MacKenzie IA, Manney GL, Chipperfield MP, Bernath PF, Walker KA, Boone CD, Froidevaux L, Livesey NJ, Waters JW. 2008. A study of stratospheric chlorine partitioning based on new satellite measurements and modeling. *J. Geophys. Res.* **113**: D12307.

Singleton CS, Randall CE, Chipperfield MP, Davies S, Feng W, Bevilacqua RM, Hoppel KW, Fromm MD, Manney GL, Harvey VL. 2005. 2002–2003 Arctic ozone loss deduced from POAM III satellite observations and the SLIMCAT chemical transport model. *Atmos. Chem. Phys.* **5**: 597–609.

Singleton CS, Randall CE, Harvey VL, Chipperfield MP, Feng W, Manney GL, Froidevaux L, Boone CD, Bernath PF, Walker KA, McElroy CT, Hoppel KW. 2007. Quantifying Arctic ozone loss during the 2004–05 winter using satellite observations and a chemical transport model. *J. Geophys. Res.* **112**: D07304, DOI: 10.1029/2006JD007463.

Urban J, Murtagh D, Lautié N, Dupuy E, de La Noë J, Eriksson P, Frisk U, Jones A, Le Flochmoën E, Olberg M, Ricaud P, Rösevall J. 2006. Odin/SMR Limb Observations of Trace Gases in the Polar Lower Stratosphere during 2004-2005. *Proc. ESA Atmospheric Science Conference, 8-12 May 2006, Frascati, Italy*. European Space Agency publications, ESA-SP-628. http://earth.esrin.esa.it/workshops/atmos2006/participants/68/paper_frascati2006.pdf.

von Hobe M, Ulanovsky A, Volk CM, Grooss J-U, Tilmes S, Konopka P, Günther G, Werner A, Spelten N, Shur G, Yushkov V, Ravegnani F, Schiller C, Müller R, Stroh F. 2006. Severe ozone depletion in the cold Arctic winter 2004–05. *Geophys. Res. Lett.* **33**: L17815, DOI: 10.1029/2006GL026945.

von Hobe M, Salawitch RJ, Canty T, Keller-Rudek H, Moortgat GK, Grooss JU, Muller R, Stroh F. 2007. Understanding the kinetics of the ClO dimer cycle. *Atmos. Chem. Phys.* **7**: 3055–3069.

WMO. 2006. *Scientific Assessment of ozone depletion: 2006*. World Meteorological Organization: Geneva.

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