On the unexplained stratospheric ozone losses during cold Arctic Januaries

Markus Rex¹, Ross J. Salawitch², Michelle L. Santee², Joe W. Waters², Karl Hoppel³, Richard Bevilacqua³

¹Alfred Wegener Institute for Polar and Marine Research, Potsdam, Germany
²Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA
³Naval Research Laboratory, Washington, DC

Abstract. Using a combination of data from Match, POAM II, POAM III and MLS we show that the chemical loss rate of Arctic O₃ during January of four cold winters (1992, 1995, 1996, and 2000) is consistently faster than can be accounted for by assuming complete activation of reactive chlorine and standard reaction kinetics. However, O₃ loss rates measured during late February and early March 1996 are shown to be consistent with observations of ClO. The faster than expected O₃ loss rates during January are shown to occur when air parcels are illuminated at high solar zenith angles (SZAs between ~85 and 94°), and to result in cumulative O₃ loss of ~0.5 ppmv. The cause of the rapid January O₃ loss is unclear, but may be related to a photolytic process at high SZA that is poorly represented by current photochemical models.

1. Introduction

Proper understanding of the timing and extent of chemical depletion of Arctic O₃ during winter is a prerequisite for developing reliable assessments of future ozone. Early studies suggested consistency between observed rates of chemical O₃ loss (hereafter referred to as O₃ loss_obs) and modeled loss rates (O₃ loss_model) based on measured concentrations of ClO and BrO and relevant laboratory kinetics [e.g., Salawitch et al., 1990]. These studies focused primarily on the February to March time period and were limited by large (e.g., factor of two) uncertainties in O₃ loss_obs [Schoeberl et al., 1990]. Several recent studies suggest that observed rates of chemical loss of Arctic O₃ are considerably faster than expected. Becker et al. [1998, 2000] reported that O₃ loss_obs for mid-January was more than a factor of two greater than loss rates found using a parcel-trajectory photochemical model. Hansen et al. [1997] reported that the accumulated O₃ loss observed at 69.3°N in late March 1996 was ~50% larger than values calculated using a chemical transport model (CTM). A similar discrepancy has been reported based on analyses of O₃ from the POAM (Polar Ozone and Aerosol Measurement) II satellite instrument using a different CTM [Deniel et al., 1998].

Using a combination of data from the Match technique, POAM II, POAM III and the Microwave Limb Sounder (MLS), we show that Arctic ozone loss rates during cold
Arctic Januaries are consistently faster than is currently understood. Our study focuses on \(O_3\) loss rates measured by the Match technique [e.g., Rex et al., 1993, 1997, 2002; von der Gathen, 1995] for four cold Arctic winters that underwent significant chemical ozone depletion during January. We use a simple theoretical framework for modeling chemical ozone loss rates [Salawitch et al., 1993] that is based on abundances of \(\text{ClO}\) specified either from MLS satellite observations [Santee et al., 1996] or by assumptions regarding the level of chlorine activation. We investigate the consistency between \(O_3\) loss \(_{\text{obs}}\) and \(O_3\) loss \(_{\text{mdl}}\) for different time periods of Arctic winter.

2. Chemical Loss of Arctic Ozone: January

Fig. 1 shows values of \(O_3\) loss \(_{\text{obs}}\) on isentropic surfaces of the lower stratosphere found by the Match technique for four winters that underwent significant chemical loss. These measurements are based on data collected by ozonesondes from dozens of stations in a coordinated manner that allows air masses to be sampled multiple times as they traverse the vortex [e.g., Rex et al., 1998, 1999]. The loss rates are expressed in ppbv/sunlit hour, a convenient way to account for variations in solar insolation. The sunlit times are defined as periods at solar zenith angles (SZA) less than 95°. The discussion in this section focuses on ozone loss rates for January of each winter.

Chemical loss of \(O_3\) per sunlit hour peaks in January of all winters due to greater abundances of \(\text{ClO}\) [Rex et al., 1997, 2002]. Data for January 1995 and 2000 are shown for the isentropic surfaces that experienced the largest ozone loss rates (490 and 500 K respectively). For 1992 and 1996, sufficient numbers of ozonesonde observations are not available to precisely define loss rates above 475 K. Therefore, for those years, ozone loss rates at the 475 K level are given in Fig. 1.

As noted above, Becker et al. [1998, 2000] could not account for the rapidity of ozone loss during January 1992 (at 475 K) and January 1995 (at 490 K). They used a Lagrangian photochemical box model with a comprehensive description of gas phase and heterogeneous reactions.

To our knowledge, during the cold Arctic Januaries discussed here, measurements of \(\text{ClO}\) at the required altitudes are not available, or not sufficiently frequent, to constrain model runs along the trajectories used in Match. Therefore we have chosen a different approach. To illustrate the extent of the discrepancy, we have used a photochemical box model to calculate the level of \(\text{ClO}\) \((\text{CIO}+2\times\text{ClOOCI})\) that would be required to account for the observed \(O_3\) loss rates along Match trajectories. In the model we use a simple theoretical framework for the representation of the diurnal variation of \(\text{ClO}, \text{ClOOCI}, \text{OCIO}, \text{BrO}, \text{BrCl}, \text{and atomic O [Salawitch et al., 1993]}\) (note 1). The calculations assume constant \(\text{ClO}\) along each Match trajectory, account for the effects of variations in temperature and solar insolation on \(O_3\) loss \(_{\text{mdl}}\), and use kinetic parameters from JPL00-3 [Sander et al., 2000] (note 2).

The level of \(\text{ClO}\) necessary to account for the observed ozone loss rates in January exceeds 5 ppbv for each winter analyzed. This is larger than 3.7 ppbv, the total amount of inorganic chlorine present in the stratosphere [WMO, 1998].
Ozone loss rates for January found by assuming ClO, equals 3.7 ppbv are also shown in Fig. 1. The failure to fully account for O₃ \textit{loss}_{\text{obs}} even assuming complete activation of ClOₓ is robust for reasonable uncertainties in the reaction coefficients of the primary ozone loss cycles (ClO+ClO and BrO+ClO). These analyses suggest that loss of O₃ in January occurs by a process that is not well represented by current photochemical models.

The discrepancy between O₃ \textit{loss}_{\text{obs}} and O₃ \textit{loss}_{\text{mdl}} is significant considering the uncertainty in the measured loss rates. The error bars for O₃ \textit{loss}_{\text{obs}} in Fig. 1 represent 1σ statistical uncertainties assuming a Gaussian distribution of the error of individual Match events (note 3). Observed ozone loss rates exceed the maximum possible modeled loss rate (assuming ClOₓ=3.7 ppbv) by 2σ to 3σ for late January 1992 and by 1σ to 2σ for parts of mid to late January of other years. Our assessment that this discrepancy is significant is based also on the consistent observation of faster than expected ozone loss rates for all cold Januaries during the past decade. Finally, the Match observation of essentially zero rates of chemical O₃ loss for January of warm winters (e.g., 1998 and 1999) [Schulz et al., 2001], when higher levels of planetary wave activity pose greater challenges to the Match approach than for cold winters, increases our confidence in the validity of the observed January loss rates shown here.

A statistical analysis of the ozonesonde data has been performed to determine whether sunlight exposure is associated with chemical ozone loss. A bivariate linear regression has been applied to the data, allowing for different rates of ozone change for the sunlit and dark (defined as SZA > 95°) segments of the trajectories [Rex et al., 1999]. Ozone depletion, expressed in units of ppbv/hr, is found only for the sunlit segments (Fig. 2). No significant change in O₃ is found for the times the airmasses are in complete darkness. The consistency of these results for four winters suggests that the unaccounted for ozone loss process is photolytic.

Since Match results are available for a range of potential temperature surfaces, the accumulated loss of ozone can be calculated on surfaces that follow the diabatic descend of air [Rex et al., 1997]. For 1994/1995 and 1999/2000 the range of theta levels for which Match results are available is sufficiently broad to do the accumulation on various descending surfaces, resulting in a vertical profile of the overall loss at the end of January (Fig. 3).

Accumulated O₃ loss measured by POAM II and POAM III for January 1995, 1996, and 2000, found by allowing vortex averaged ozone to descend using calculated cooling rates [Hoppel et al., 2002], compares well with Match observations considering the respective uncertainties (Fig. 3).

Significant chemical removal of O₃ during January has been reported by other techniques. Accumulated chemical loss of 0.5 ppmv of ozone at 465 K was observed by MLS during January 1995 (Fig. 3), in excellent quantitative agreement with ozone reductions found by Match [Harris et al., 2002]. In January 2000 ozone loss derived by Match peaks at ~0.54 ± 0.2 ppmv between potential temperature levels of 480 and 520 K. Accumulated loss of O₃ was moderate (~0.22 ± 0.13 ppmv) at the 444 K surface, close to the cruise altitude of the
NASA ER-2 aircraft during January. Therefore, the finding of little or no chemical loss of ozone (0.0 ± 0.15 ppmv) from ER-2 observations during January 2000 [Richard et al., 2001] is not inconsistent with the analyses presented here.

3. Chemical Loss of Arctic Ozone: February and March

Changes in ozone per sunlit hour are smaller in February and March compared to January because of partial recovery of ClO, to the CINO₃ reservoir [Rex et al., 1997, 2002]. In this section, we use MLS observations of ClO to calculate loss rates along the Match trajectories, and compare them to Match estimates of O₃ loss.₃

1996 is the only year for which Match observations of rapid ozone loss overlapped with sufficiently dense MLS observations of ClO to allow the reconstruction of ClO along the match trajectories. MLS observations during rapid ozone loss events in other years were not available due to the monthly yaw of the Upper Atmospheric Research Satellite (UARS) or were not sufficiently dense due to difficulties with the MLS scan mechanism in later years.

We have reconstructed the abundance of active chlorine along the Match trajectories by interpolating between mixing ratios of ClO, that have been inferred from MLS measurements of ClO close to the respective trajectories. We use Version 5 MLS retrievals, which provide a better definition of the vertical distribution of ClO than previous MLS retrievals [Livesey et al., 2002]. O₃ loss was calculated along each Match trajectory at 475 K for this time period. All other assumptions (i.e., BrO, O₃) are as previously described. Excellent agreement is found between decreases in O₃ along the Match trajectories and modeled loss based on MLS observations of ClO for late February/early March 1996 (Fig. 4). The ozone loss rates (e.g., change per sunlit hour) are considerably slower than observed during January. Abundances of ClO, inferred from MLS ClO along Match trajectories range from ~1.2 to 2.6 ppbv. Most importantly, the Match trajectories spend a considerably smaller portion of their overall sunlit time at high SZA (e.g., between ~85 and 94°) than is found for the January trajectories.

4. Discussion

We turn our attention to speculation regarding the cause of the rapid ozone loss during January. Standard photochemical models predict relatively slow rates of polar O₃ loss at high SZA (e.g., between 85 and 94°) because strong attenuation of UV light, due to the high O₃ slant columns, limits the photolysis rate of ClOOCl and hence the overall rate of O₃ loss by the ClO+ClO and BrO+ClO cycles. Prior to the SOLVE/THESEO 2000 field campaign, we had speculated that photolysis of ClOOCl by an unknown state in the near IR (wavelengths > 800 nm, which is optically thin even at high SZA) might provide a strong enhancement to the abundance of Cl and ClO during twilight. Such photolysis could lead to significant increases in chemical ozone loss rates at high SZA. Little change would occur for calculated loss
along trajectories in late February and early March because air parcels spend a much smaller fraction of overall sunlit time at high SZA. However, in-situ observations of ClO and ClOOCl, obtained from the NASA ER-2 during SOLVE, provide evidence that ClOOCl does not photolyze at an appreciable rate in the near IR [R. M. Stimpfle, private communication, 2002]. Hence, we are left to ponder other possible causes of the observed rapid loss of ozone during January.

It is possible that O₃ is lost by reactions on the surface of PSCs (polar stratospheric clouds). The upper limit for the reaction probability of this process, 2.5×10⁻⁴ on the surface of nitric acid trihydrate [Sander et al., 2000], suggests that this process could contribute significantly to ozone loss in January. For each January considered here, air was exposed to considerable amounts of PSCs during both day and night. Our finding that loss of ozone occurs only during sunlit periods suggests that, if direct loss on PSC surfaces is responsible, such loss must be driven by photons. Observations indicate that BrO does not fall off with increasing SZA near sunset as rapidly as expected [Wahner and Schiller, 1992; Avallone and Toohey, 2001]. It is difficult to reconcile these observations with existing photochemical theory. Nonetheless, it is not clear how enhanced BrO in twilight could lead to appreciable increases in chemical loss rates since ClO is observed to decline with increasing SZA essentially as expected [Kreher et al., 2002; R. M. Stimpfle, private communication, 2002]. A reactive partner is required for the enhanced levels of BrO, since the self-reaction of BrO is too slow to contribute appreciable amounts of ozone loss. Perhaps loosely bound higher oxides of ClOOCl contribute to the rapid ozone loss found in January, either by reaction with BrO or in other yet unidentified ozone loss cycles [Sander et al., 1989]. Better understanding of the photochemistry of this time period requires observations at high SZA, and appropriate potential temperature levels (e.g., 480 to 520 K), of BrO, other radicals, and a variety of chlorine species to test the budget and partitioning of halogens in the stratosphere.

5. Concluding Remarks

We have analyzed data from Match, POAM II, POAM III and MLS to assess our understanding of Arctic ozone loss rates. The consistent inability to fully account for observed ozone loss rates during cold Arctic Januaries suggests the existence of a currently unknown ozone loss mechanism. Detailed data analyses indicate that this loss process involves a photolytic step. Observed ozone loss later during winter (e.g., mid February to early March) is in good quantitative agreement with model results based on observed ClO, suggesting that the unknown ozone loss mechanism is most important at high SZA and low temperatures typical of January conditions.

During cold Arctic Januaries we find cumulative ozone loss of about 0.5 ppmv. Although our and other analyses point toward the existence of a currently unknown ozone loss mechanism, its relative impact is modest for winters with massive ozone depletion. For such winters, loss of ozone predominantly occurs during February and March by known catalytic processes (ClO+ClO and ClO+BrO) that operate...
efficiently under conditions of high solar illumination. Nonetheless, the January discrepancy demands further investigation because reliable assessments of future Arctic ozone depletion require a full understanding of all significant processes that affect ozone.

Acknowledgments. We have benefited from public discussion of this material at the Arctic Ozone Workshop held in Potsdam, Germany during March 2002. Research at the Jet Propulsion Laboratory (JPL), California Institute of Technology, is performed under contract with the National Aeronautics and Space Administration. This work was initiated when M. Rex was at JPL, supported by the NASA UARS Guest Investigator Program. Work at the Alfred Wegener Institute was supported by the BMBF under the project AFO 2000/07ATC08.

Notes

1. Values of BrO are found by specifying the sum, BrO+BrCl, as a function of potential temperature such that observed mixing ratios of BrO in the Arctic vortex [Harder et al., 1998] are reproduced. Measurements of O₃ from Match are also specified along each trajectory.

2. Use of the Bloss et al. (2001) rate for ClO+ClO+M rather than the JPL00-3 [Sander et al., 2000] rate has essentially no effect on our model calculations because a faster rate titrates ClO into ClOOCl. Hence, the increase in O₃ loss due to the ClO+ClO cycle is nearly balanced by the calculated decrease due to the BrO+ClO cycle.

3. An analysis of the individual errors of the Match events shows that the distribution of errors is Gaussian [Rex, 1993]. However, based on the sample size, it is hard to exclude a small, non-Gaussian component at the far edge (e.g., beyond 2σ) of the distribution. Since faster than expected ozone loss rates are observed for all cold Januaries, it is unlikely that the discrepancy discussed in this paper is due to a statistical fluctuation of the data.

References


Kreher et al., 2002.


Figure 1. Chemical loss rate of O3 (O3 loss_obs) in the Arctic vortex for indicated years and isentropic surfaces based on the Match method (red boxes; error bars represent 1σ uncertainty). The abundance of ClO necessary to account for O3 loss_obs along each trajectory (green dots; see text) for JPL00-3 kinetics is also shown. Also shown is an estimate of O3 loss_mdl for January of each year assuming ClO_x=3.7 ppbv (blue dashed line).

Figure 2. Rate of change of ozone along Match trajectories for data collected during sunlit conditions (defined as SZA < 95°) and during dark periods (SZA > 95°) based on bivariate regressions for data collected between 5 and 31 January of each year for the set of matches used in Fig. 1. Error bars are 1σ estimates of the statistical uncertainty. During January 1996 a much smaller number of ozone soundings have been performed compared to the other years shown here and the uncertainty of the bivariate analysis is much larger.

Figure 3. Accumulated chemical loss of O3 versus potential temperature for January of 1992 (black), 1995 (red), 1996 (green), and 2000 (blue). Results from Match analyses are shown by solid lines with solid markers. The single open marker represents a result from MLS for 1 to 31 January 1995 [Harris et al., 2002]. The dotted lines represent ozone losses derived from POAM II and III measurements. For these an ozone versus PV relation was derived from POAM.
measurements made during day $32 \pm 2$ days. The vortex average ozone profile was calculated based on these relations at various heights. The ozone loss was then estimated by comparing this profile with subsided vortex average profiles calculated with the same approach for day $5 \pm 2$ days. Error bars represent $1\sigma$ uncertainties.

Fig. 4. The chemical loss of O$_3$ measured by Match between 20 February 1996 and 3 March 1996 at 475 K versus the amount of sunlight exposure along each Match trajectory (red squares) and the computed reduction in O$_3$ along the same Match trajectory based on MLS Version 5 measurements of ClO (green crosses). Error bars represent the $1\sigma$ sigma standard deviation of the measured and modeled changes in O$_3$. 
Figure 1, Rex et al.
Rate of ozone reduction along trajectories [ ppbv / h ]

- Night (sun below horizon)
- Day (sun above horizon)

Figure 2, Rex et al.
Figure 3, Rex et al.
Red: measured
- $2.8 \pm 0.7$ ppbv / sunlit hour

Green: model constrained by MLS ClO
- $2.9 \pm 0.1$ ppbv / sunlit hour

Figure 4, Rex et al.