On the unexplained stratospheric ozone losses during cold Arctic Januaries

M. Rex,[1] R. J. Salawitch,[2] M. L. Santee,[2] J. W. Waters,[2] K. Hoppel,[3] and R. Bevilacqua[3]

[1] Using a combination of data from Match, POAM II, POAM III and MLS we show that the chemical loss rate of Arctic O_3 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, O_3 loss rates measured during late February and early March 1996 are shown to be consistent with observations of ClO. The faster than expected O_3 loss rates during January are shown to occur when air parcels are illuminated at high solar zenith angles (SZAs between $\sim$85 and 94°), and to result in cumulative O_3 loss of $\sim$0.5 ppmv. The cause of the rapid January O_3 loss is unclear, but may be related to a photolytic process at high SZA that is poorly represented by current photochemical models. *INDEX TERMS:* 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325); 3337 Meteorology and Atmospheric Dynamics: Numerical modeling and data assimilation; 9315 Information Related to Geographic Region: Arctic region. **Citation:** Rex, M., R. J. Salawitch, M. L. Santee, J. W. Waters, K. Hoppel, and R. Bevilacqua, On the unexplained stratospheric ozone losses during cold Arctic Januaries, *Geophys. Res. Lett.*, *30*(1), 1008, doi:10.1029/2002GL016008, 2003.

1. Introduction

[2] Proper understanding of the timing and extent of chemical depletion of Arctic O_3 is a prerequisite for developing reliable assessments of future ozone abundances. Early studies suggested consistency between *observed* rates of chemical O_3 loss (hereafter referred to as $O_3 loss\_obs$) and *modeled* loss rates ($O_3 loss\_mdl$) based on measured concentrations of ClO and BrO and relevant laboratory kinetics [e.g., *Salawitch et al.*, 1990]. These studies focused primarily on February to March and were limited by large (e.g., factor of two) uncertainties in $O_3 loss\_obs$ [*Schoeberl et al.*, 1990].

[3] Several recent studies suggest that observed rates of chemical loss of Arctic O_3 are considerably faster than expected during mid-winter [e.g., *Becker et al.*, 1998; *Hansen et al.*, 1997; *Deniel et al.*, 1998].

[4] 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 during cold Arctic Januaries is consistently faster than is currently understood. Our study focuses on four cold Arctic winters that experienced significant chemical ozone depletion during January.

2. Chemical Loss of Arctic Ozone: January

[5] Figure 1 shows values of $O_3 loss\_obs$ on isentropic surfaces of the lower stratosphere found by the Match technique. 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 SVA $<\sim$95°.

[6] Chemical loss of O_3 per sunlit hour peaks in January of all winters due to greater abundances of ClO_x [*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 Figure 1.

[7] We have used a photochemical box model to calculate the level of ClO_x (ClO + 2 $\times$ ClOOCl) 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 ClO, ClOOCl, OClO, BrO, BrCl, and atomic O [*Salawitch et al.*, 1993]. 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 [*Avallone et al.*, 1995] are reproduced. Measurements of O_3 from Match are also specified along each trajectory. The calculations assume constant ClO_x along each Match trajectory, account for the effects of variations in temperature and solar insolation and use kinetic parameters from JPL00-3 [*Sander et al.*, 2000]. Use of the *Bloss et al.* [2001] rate for ClO + ClO + M has little effect on our model calculations because a faster rate titrates ClO into ClOOCl and the increase in O_3 loss due to the ClO + ClO cycle is nearly balanced by a slowing down of the BrO + ClO cycle.

[8] The level of ClO_x 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_x equals 3.7 ppbv are also shown in Figure 1. The failure to fully account for $O_3 loss\_obs$, even assuming complete activation of ClO_x, is robust for reasonable uncertainties in the reaction coefficients of the primary ozone loss cycles (ClO + ClO and BrO + ClO). These analyses suggest

[1]Alfred Wegener Institute for Polar and Marine Research, Potsdam, Germany.
[2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA.
[3]Naval Research Laboratory, Washington, DC, USA.
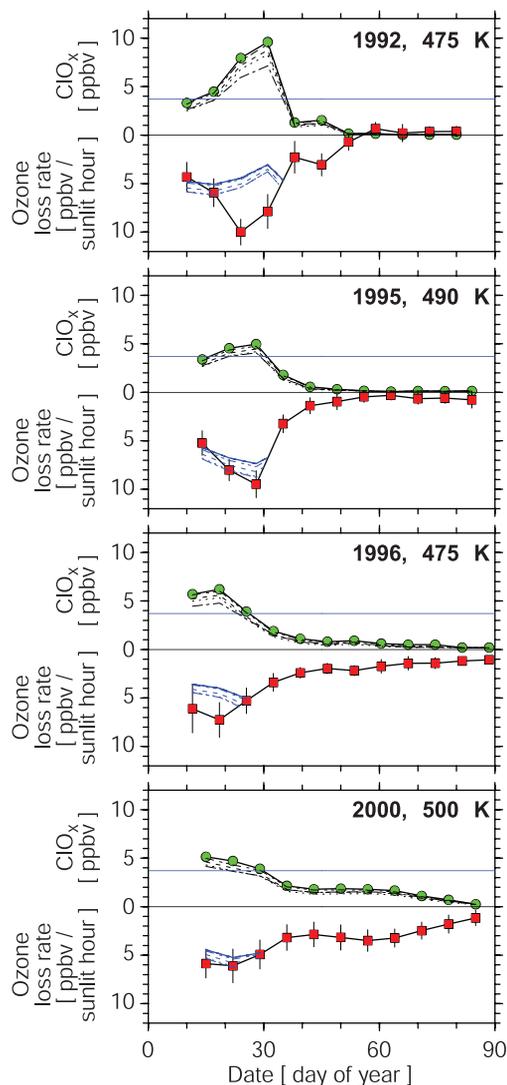
Figure 1. Chemical loss rate of O_3 (O_3 *loss_obs*) in the Arctic vortex based on Match (red boxes; error bars are 1σ uncertainty). The abundance of ClO_x necessary to account for O_3 *loss_obs* (green dots) and an estimate of O_3 *loss_mdl* for January of each year assuming ClO_x = 3.7 ppbv (horizontal blue line) are also shown. Dashed lines: BrO_x based on measurements of BrO by Pfeilsticker et al. (private communication) (run 1). Dotted lines: These values for BrO_x plus 20% (run 2). Dash-dotted lines: J_{Cl2O2} plus 50% (run 3). Dash-dot-dotted lines: $k_{ClO+ClO}$ plus 30% (run 4). Run 2 and 3 are the lines farthest from the base run, run 4 lies closest to it.

that loss of O_3 in January occurs by a process that is not well represented by current models.

[9] Observed ozone loss rates exceed the maximum possible modeled loss rate (assuming ClO_x = 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.

[10] The model calculations depend on the abundance of BrO_x, the photolysis rate of Cl_2O_2 (J_{Cl2O2}) and the constant rate for the reaction $ClO + ClO + M$ ($k_{ClO+ClO}$). We have varied these parameters within reasonable limits, i.e. for BrO the highest measurements of bromine

reported for the Arctic so far (Pfeilsticker et al., private communication) plus 20%, these runs were designed to encompass uncertainties in both BrO and $K_{BrOTClO}$ for $k_{ClO+ClO}$ the uncertainty given in JPL00-3 (which encompasses the values reported by *Bloss et al.* [2001]), and for J_{Cl2O2} the recommended value ±50%. The results of some of these sensitivity studies are given in Figure 1. For some of the points in January the discrepancy is larger than the combined uncertainties of the model results and the observations. 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. However, the uncertainty for J_{Cl2O2} given in JPL00-3 at 50 hPa is about a factor of three. Using the upper limit of J_{Cl2O2} based on this uncertainty, all measurements fall within the model uncertainty, with the exception of two points in January 1992. But increasing J_{Cl2O2} by a factor of three would not be consistent with analysis of ClO measurements at high SZA [e.g. *Avallone and Toohey*, 2001; *Vömel et al.*, 2001], which suggest that the 50% used here is a more realistic estimate for the uncertainty. Finally, the Match observation of essentially zero rates of chemical O_3 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.

[11] A bivariate linear regression has been applied to the data to determine whether sunlight exposure is associated with chemical ozone loss [*Rex et al.*, 1999]. Ozone depletion is found only for the sunlit segments along the trajectories (Figure 2). No significant change in O_3 is found for complete darkness. The consistency of these results for four winters suggests that the unaccounted for ozone loss process is photolytic.

[12] 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 a vertical profile of the overall loss at the end of January (Figure 3) can be derived from the Match results. Accumulated O_3 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 (Figure 3). Significant chemical removal of O_3 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 (Figure 3), in excellent quantitative agreement with ozone reductions found by Match [*Harris et al.*, 2002].

[13] In January 2000 accumulated loss of O_3 was ($\sim$0.22 ± 0.13 ppmv) at the cruise altitude of the NASA ER-2 aircraft during January, consistent with 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].

3. February and March

[14] Changes in ozone per sunlit hour are smaller in February and March compared to January because of partial
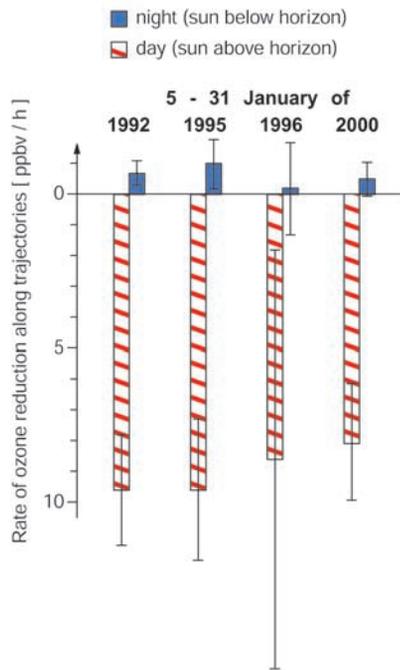
Figure 2. Rate of change of ozone along Match trajectories during sunlit conditions and during dark periods based on bivariate regressions for data collected between 5 and 31 January of each year for the set of matches used in Figure 1. Error bars are 1σ statistical uncertainties. During January 1996 a smaller number of ozone soundings have been performed and the uncertainty of the bivariate analysis is much larger.

recovery of ClO_x to the $ClNO_3$ 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 O_3 loss_obs.

[15] 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_x along the Match trajectories. MLS observations during rapid ozone loss 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.

[16] We have reconstructed the abundance of ClO_x along the Match trajectories by interpolating between mixing ratios of ClO_x 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]. O_3 loss_mdl was calculated along each Match trajectory at 475 K for this time period. All other assumptions (i.e., BrO_x, O_3) are as previously described.

[17] Excellent agreement is found between the observed and modeled loss rates for late February/early March 1996 (Figure 4). The ozone loss per sunlit hour) is considerably smaller than during January. Abundances of ClO_x 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
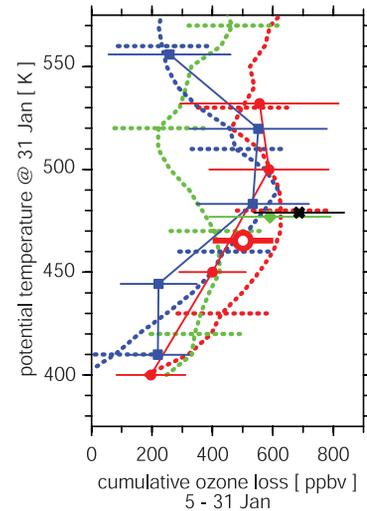

Figure 3. Accumulated chemical loss of O_3 versus potential temperature for 5−31 January of 1992 (black), 1995 (red), 1996 (green), and 2000 (blue), as derived by various methods: Match (solid lines with solid markers), MLS (single open marker) [*Harris et al.*, 2002] and POAM (dotted lines). For the latter an ozone versus PV relation was derived from measurements made during day 32 ± 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 ± 2 days. Error bars represent 1σ uncertainties.

at high SZA (e.g., between ∼85 and 94°) than during January.

4. Discussion

[18] Standard photochemical models predict relatively slow rates of polar O_3 loss at high SZA (e.g., between 85 and 94°) because strong attenuation of UV light, due to the high O_3 slant columns, limits the photolysis rate of ClOOCl and hence the overall rate of O_3 loss by the ClO + ClO and BrO + ClO cycles.
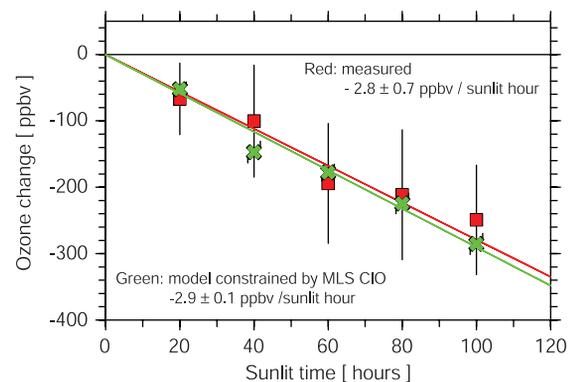
Figure 4. The chemical loss of O_3 measured by Match between 20 February and 3 March 1996 at 475 K versus the amount of sunlight exposure along each Match trajectory (red squares) and the computed reduction in O_3 along the same trajectory based on MLS Version 5 measurements of ClO (green crosses). Error bars are 1σ sigma standard deviations.

[19] Longwave photolysis of ClOOCl by an unknown state in the near IR (wavelengths > 800 nm, which is optically thin even at high SZA) could principally provide a strong enhancement to the abundance of Cl and ClO during twilight and hence faster ozone loss. However, in-situ observations of ClO provide evidence that ClOOCl does not photolyze at an appreciable rate in the near IR [*Avallone and Toohey*, 2001; *Vömel et al.*, 2001; R. M. Stimpfle, private comm., 2002].

[20] O_3 could also be 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.

[21] 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]. But 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 [*Vömel et al.*, 2001 at sunrise. Observations of a burst of ClO at sunrise [*Pierson et al.*, 1999] and unusually high amounts of BrO at twilight [*Avallone and Toohey*, 2001] suggest that halogen chemistry at high SZA is not fully understood. 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 more extensive 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

[22] 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 analyses suggest that this loss process involves a photolytic step. The lack of measurable loss during warm winters indicates that the process is related to ClO_x and/or PSCs. Observed ozone loss later during winter is in good 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.

[23] During cold Arctic Januaries we find cumulative ozone loss of about 0.5 ppmv. This is modest for winters with massive ozone depletion. For such Arctic winters, loss of ozone predominantly occurs during February and March by known catalytic processes 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.

References

Avallone, L. M., and D. W. Toohey, Tests of halogen photochemistry using in situ measurements of ClO and BrO in the lower polar stratosphere, *J. Geophys. Res.*, *106*, 10,411–10,421, 2001.

Avallone, L. M., D. W. Toohey, and K. R. Chan, In situ measurements of BrO during AASE II, *Geophys. Res. Lett.*, *22*, 831, 1995.

Becker, G., et al., Ozone loss rates in the Arctic stratosphere in the winter 1991/92: Model calculations compared with Match results, *Geophys. Res. Lett.*, *25*, 4325–4328, 1998.

Bloss, W. J., et al., Kinetics of the ClO self reaction and 210 nm absorption cross section of the ClO dimer, *J. Phys. Chem. A.*, *105*, 11,226–11,239, 2001.

Deniel, C., et al., Arctic chemical ozone depletion during the 1994–1995 winter from POAM II observations and the REPROBUS 3D model, *J. Geophys. Res.*, *103*, 19,231–19,244, 1998.

Hansen, G., et al., Evidence of substantial O_3 depletion in winter 1995/96 over Norway, *Geophys. Res. Lett.*, *24*, 799–802, 1997.

Harris, N. R. P., et al., Comparison of empirically derived ozone losses in the Arctic vortex, *J. Geophys. Res.*, in press, 2002.

Hoppel, K., et al., POAM III observations of Arctic ozone loss for the 1999/2000 winter, *J. Geophys. Res.*, *25*, in press, 2002.

Livesey, N. J., et al., The UARS Microwave Limb Sounder version 5 data set: Theory, characterization and validation, submitted to *J. Geophys. Res.*, 2002.

McKinney, K. A., J. M. Pierson, and D. W. Toohey, A winter time in-situ profile of BrO between 17 and 27 km in the Arctic vortex, *Geophys. Res. Lett.*, *24*, 853, 1997.

Pierson, J. M., K. A. McKinney, D. W. Toohey, J. Margitan, U. Schmidt, A. Engel, and P. A. Newman, An investigation of ClO photochemistry in the chemically perturbed Arctic vortex, *J. Atmos. Chem.*, *32*, 61, 1999.

Rex, M., et al., Prolonged stratospheric ozone loss in the 1995–96 Arctic winter, *Nature*, *389*, 835–838, 1997.

Rex, M., et al., In situ measurements of stratospheric ozone depletion rates in the Arctic winter 1991/1992: A Lagrangian approach, *J. Geophys. Res.*, *103*, 5843–5853, 1998.

Rex, M., et al., Chemical ozone loss in the Arctic winter 1994/95 as determined by Match, *J. Atmos. Chem.*, *32*, 35–59, 1999.

Rex, M., et al., Chemical depletion of Arctic ozone in winter 1999/2000, *J. Geophys. Res.*, in press, 2002.

Richard, E., et al., Severe chemical ozone loss inside the Arctic polar vortex during winter 1999–2000 inferred from in situ airborne measurements, *Geophys. Res. Lett.*, *28*, 2197–2200, 2001.

Salawitch, R. J., et al., Loss of ozone in the Arctic vortex for the winter of 1989, *Geophys. Res. Lett.*, *17*, 561–564, 1990.

Salawitch, R. J., et al., Chemical loss of ozone in the Arctic polar vortex in the winter of 1991–92, *Science*, *261*, 1146–1149, 1993.

Sander, S. P., R. R. Friedl, and Y. L. Yung, Rate of formation of the ClO dimer in the polar stratosphere: Implications for ozone loss, *Science*, *245*, 1095–1098, 1989.

Sander, S. P., et al., Chemical kinetics and photochemical data for use in stratospheric modeling, JPL Public. 00-3, Pasadena, CA, 2000.

Schoeberl, M. R., et al., Stratospheric constituent trends from ER-2 profile data, *Geophys. Res. Lett.*, *17*, 469–472, 1990.

Schulz, A., et al., Arctic ozone loss in threshold conditions: Match observations in 1997/98 and 1998/99, *J. Geophys. Res.*, *106*, 7495–7504, 2001.

Vömel, H., D. W. Toohey, T. Deshler, and C. Kröger, Sunset observations of ClO in the Arctic polar vortex and implications for ozone loss, *Geophys. Res. Lett.*, *28*, 4183–4186, 2001.

———————

M. Rex, Alfred Wegener Institute for Polar and Marine Research, Potsdam, Germany.

R. J. Salawitch, M. L. Santee, and J. W. Waters, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

K. Hoppel and R. Bevilacqua, Naval Research Laboratory, Washington, DC, USA.