

# 1 On the unexplained stratospheric ozone losses during cold 2 Arctic Januaries

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9 **Abstract.** Using a combination of data from Match, POAM II,  
10 POAM III and MLS we show that the chemical loss rate of  
11 Arctic O<sub>3</sub> during January of four cold winters (1992, 1995,  
12 1996, and 2000) is consistently faster than can be accounted  
13 for by assuming complete activation of reactive chlorine and  
14 standard reaction kinetics. However, O<sub>3</sub> loss rates measured  
15 during late February and early March 1996 are shown to be  
16 consistent with observations of ClO. The faster than expected  
17 O<sub>3</sub> loss rates during January are shown to occur when air  
18 parcels are illuminated at high solar zenith angles (SZAs  
19 between ~85 and 94°), and to result in cumulative O<sub>3</sub> loss of  
20 ~0.5 ppmv. The cause of the rapid January O<sub>3</sub> loss is unclear,  
21 but may be related to a photolytic process at high SZA that is  
22 poorly represented by current photochemical models.

## 23 1. Introduction

24 Proper understanding of the timing and extent of chemical  
25 depletion of Arctic O<sub>3</sub> during winter is a prerequisite for  
26 developing reliable assessments of future ozone. Early studies  
27 suggested consistency between *observed* rates of chemical O<sub>3</sub>  
28 loss (hereafter referred to as O<sub>3</sub> *loss\_obs*) and *modeled* loss rates  
29 (O<sub>3</sub> *loss\_mdl*) based on measured concentrations of ClO and  
30 BrO and relevant laboratory kinetics [e.g., Salawitch *et al.*,  
31 1990]. These studies focused primarily on the February to  
32 March time period and were limited by large (e.g., factor of  
33 two) uncertainties in O<sub>3</sub> *loss\_obs* [Schoeberl *et al.*, 1990].

34 Several recent studies suggest that observed rates of  
35 chemical loss of Arctic O<sub>3</sub> are considerably faster than  
36 expected. Becker *et al.* [1998, 2000] reported that O<sub>3</sub> *loss\_obs*  
37 for mid-January was more than a factor of two greater than  
38 loss rates found using a parcel-trajectory photochemical model.  
39 Hansen *et al.* [1997] reported that the accumulated O<sub>3</sub> loss  
40 observed at 69.3°N in late March 1996 was ~50% larger than  
41 values calculated using a chemical transport model (CTM). A  
42 similar discrepancy has been reported based on analyses of O<sub>3</sub>  
43 from the POAM (Polar Ozone and Aerosol Measurement) II  
44 satellite instrument using a different CTM [Deniel *et al.*,  
45 1998].

46 Using a combination of data from the Match technique,  
47 POAM II, POAM III and the Microwave Limb Sounder  
48 (MLS), we show that Arctic ozone loss rates during cold

1 Arctic Januaries are consistently faster than is currently  
2 understood. Our study focuses on O<sub>3</sub> loss rates measured by  
3 the Match technique [e.g., *Rex et al.*, 1993, 1997, 2002; von  
4 der Gathen, 1995] for four cold Arctic winters that underwent  
5 significant chemical ozone depletion during January. We use a  
6 simple theoretical framework for modeling chemical ozone  
7 loss rates [*Salawitch et al.*, 1993] that is based on abundances  
8 of ClO specified either from MLS satellite observations  
9 [*Santee et al.*, 1996] or by assumptions regarding the level of  
10 chlorine activation. We investigate the consistency between  
11 O<sub>3</sub> *loss\_obs* and O<sub>3</sub> *loss\_mdl* for different time periods of Arctic  
12 winter.

## 13 2. Chemical Loss of Arctic Ozone: January

14 Fig. 1 shows values of O<sub>3</sub> *loss\_obs* on isentropic surfaces of  
15 the lower stratosphere found by the Match technique for four  
16 winters that underwent significant chemical loss. These  
17 measurements are based on data collected by ozonesondes  
18 from dozens of stations in a coordinated manner that allows air  
19 masses to be sampled multiple times as they traverse the vortex  
20 [e.g., *Rex et al.*, 1998, 1999]. The loss rates are expressed in  
21 ppbv/sunlit hour, a convenient way to account for variations in  
22 solar insolation. The sunlit times are defined as periods at solar  
23 zenith angles (SZA) less than 95°. The discussion in this  
24 section focuses on ozone loss rates for January of each winter.

25 Chemical loss of O<sub>3</sub> per sunlit hour peaks in January of all  
26 winters due to greater abundances of ClO [*Rex et al.*, 1997,  
27 2002]. Data for January 1995 and 2000 are shown for the  
28 isentropic surfaces that experienced the largest ozone loss rates  
29 (490 and 500 K respectively). For 1992 and 1996, sufficient  
30 numbers of ozonesonde observations are not available to  
31 precisely define loss rates above 475 K. Therefore, for those  
32 years, ozone loss rates at the 475 K level are given in Fig. 1.

33 As noted above, *Becker et al.* [1998, 2000] could not  
34 account for the rapidity of ozone loss during January 1992 (at  
35 475 K) and January 1995 (at 490 K). They used a Lagrangian  
36 photochemical box model with a comprehensive description of  
37 gas phase and heterogeneous reactions.

38 To our knowledge, during the cold Arctic Januaries  
39 discussed here, measurements of ClO at the required altitudes  
40 are not available, or not sufficiently frequent, to constrain  
41 model runs along the trajectories used in Match. Therefore we  
42 have chosen a different approach. To illustrate the extent of the  
43 discrepancy, we have used a photochemical box model to  
44 calculate the level of ClO<sub>x</sub> (ClO+2×ClOOCl) that would be  
45 required to account for the observed O<sub>3</sub> loss rates along Match  
46 trajectories. In the model we use a simple theoretical  
47 framework for the representation of the diurnal variation of  
48 ClO, ClOOCl, OCIO, BrO, BrCl, and atomic O [*Salawitch et*  
49 *al.*, 1993] (note 1). The calculations assume constant ClO<sub>x</sub>  
50 along each Match trajectory, account for the effects of  
51 variations in temperature and solar insolation on O<sub>3</sub> *loss\_mdl*,  
52 and use kinetic parameters from JPL00-3 [*Sander et al.*, 2000]  
53 (note 2).

54 The level of ClO<sub>x</sub> necessary to account for the observed  
55 ozone loss rates in January exceeds 5 ppbv for each winter  
56 analyzed. This is larger than 3.7 ppbv, the total amount of  
57 inorganic chlorine present in the stratosphere [*WMO*, 1998].

1 Ozone loss rates for January found by assuming  $\text{ClO}_x$  equals  
2 3.7 ppbv are also shown in Fig. 1. The failure to fully account  
3 for  $\text{O}_3$  *loss\_obs*, even assuming complete activation of  $\text{ClO}_x$ , is  
4 robust for reasonable uncertainties in the reaction coefficients  
5 of the primary ozone loss cycles ( $\text{ClO}+\text{ClO}$  and  $\text{BrO}+\text{ClO}$ ).  
6 These analyses suggest that loss of  $\text{O}_3$  in January occurs by a  
7 process that is not well represented by current photochemical  
8 models.

9 The discrepancy between  $\text{O}_3$  *loss\_obs* and  $\text{O}_3$  *loss\_mdl* is  
10 significant considering the uncertainty in the measured loss  
11 rates. The error bars for  $\text{O}_3$  *loss\_obs* in Fig. 1 represent  $1\sigma$   
12 statistical uncertainties assuming a Gaussian distribution of the  
13 error of individual Match events (note 3). Observed ozone loss  
14 rates exceed the maximum possible modeled loss rate  
15 (assuming  $\text{ClO}_x=3.7$  ppbv) by  $2\sigma$  to  $3\sigma$  for late January 1992  
16 and by  $1\sigma$  to  $2\sigma$  for parts of mid to late January of other years.  
17 Our assessment that this discrepancy is significant is based  
18 also on the consistent observation of faster than expected  
19 ozone loss rates for all cold Januaries during the past decade.  
20 Finally, the Match observation of essentially zero rates of  
21 chemical  $\text{O}_3$  loss for January of warm winters (e.g., 1998 and  
22 1999) [Schulz *et al.*, 2001], when higher levels of planetary  
23 wave activity pose greater challenges to the Match approach  
24 than for cold winters, increases our confidence in the validity  
25 of the observed January loss rates shown here.

26 A statistical analysis of the ozonesonde data has been  
27 performed to determine whether sunlight exposure is  
28 associated with chemical ozone loss. A bivariate linear  
29 regression has been applied to the data, allowing for different  
30 rates of ozone change for the sunlit and dark (defined as  $\text{SZA} >$   
31  $95^\circ$ ) segments of the trajectories [Rex *et al.*, 1999]. Ozone  
32 depletion, expressed in units of ppbv/hr, is found only for the  
33 sunlit segments (Fig. 2). No significant change in  $\text{O}_3$  is found  
34 for the times the airmasses are in complete darkness. The  
35 consistency of these results for four winters suggests that the  
36 unaccounted for ozone loss process is photolytic.

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

45 Accumulated  $\text{O}_3$  loss measured by POAM II and POAM III  
46 for January 1995, 1996, and 2000, found by allowing vortex  
47 averaged ozone to descend using calculated cooling rates  
48 [Hoppel *et al.*, 2002], compares well with Match observations  
49 considering the respective uncertainties (Fig. 3).

50 Significant chemical removal of  $\text{O}_3$  during January has been  
51 reported by other techniques. Accumulated chemical loss of  
52 0.5 ppmv of ozone at 465 K was observed by MLS during  
53 January 1995 (Fig. 3), in excellent quantitative agreement with  
54 ozone reductions found by Match [Harris *et al.*, 2002].

55 In January 2000 ozone loss derived by Match peaks at  $\sim 0.54$   
56  $\pm 0.2$  ppmv between potential temperature levels of 480 and  
57 520 K. Accumulated loss of  $\text{O}_3$  was moderate ( $\sim 0.22 \pm 0.13$   
58 ppmv) at the 444 K surface, close to the cruise altitude of the

1 NASA ER-2 aircraft during January. Therefore, the finding of  
2 little or no chemical loss of ozone ( $0.0 \pm 0.15$  ppmv) from ER-  
3 2 observations during January 2000 [Richard *et al.*, 2001] is  
4 not inconsistent with the analyses presented here.

### 5 **3. Chemical Loss of Arctic Ozone: February and** 6 **March**

7 Changes in ozone per sunlit hour are smaller in February  
8 and March compared to January because of partial recovery of  
9  $\text{ClO}_x$  to the  $\text{ClNO}_3$  reservoir [Rex *et al.*, 1997, 2002]. In this  
10 section, we use MLS observations of ClO to calculate loss  
11 rates along the Match trajectories, and compare them to Match  
12 estimates of  $\text{O}_3$  *loss\_obs*.

13 1996 is the only year for which Match observations of rapid  
14 ozone loss overlapped with sufficiently dense MLS  
15 observations of ClO to allow the reconstruction of  $\text{ClO}_x$  along  
16 the match trajectories. MLS observations during rapid ozone  
17 loss events in other years were not available due to the  
18 monthly yaw of the Upper Atmospheric Research Satellite  
19 (UARS) or were not sufficiently dense due to difficulties with  
20 the MLS scan mechanism in later years.

21 We have reconstructed the abundance of active chlorine  
22 along the Match trajectories by interpolating between mixing  
23 ratios of  $\text{ClO}_x$  that have been inferred from MLS  
24 measurements of ClO close to the respective trajectories. We  
25 use Version 5 MLS retrievals, which provide a better definition  
26 of the vertical distribution of ClO than previous MLS retrievals  
27 [Livesey *et al.*, 2002].  $\text{O}_3$  *loss\_mdl* was calculated along each  
28 Match trajectory at 475 K for this time period. All other  
29 assumptions (i.e.,  $\text{BrO}_x$ ,  $\text{O}_3$ ) are as previously described.<sup>1</sup>

30 Excellent agreement is found between decreases in  $\text{O}_3$  along  
31 the Match trajectories and modeled loss based on MLS  
32 observations of ClO for late February/early March 1996 (Fig.  
33 4). The ozone loss rates (e.g., change per sunlit hour) are  
34 considerably slower than observed during January.  
35 Abundances of  $\text{ClO}_x$  inferred from MLS ClO along Match  
36 trajectories range from  $\sim 1.2$  to  $2.6$  ppbv. Most importantly, the  
37 Match trajectories spend a considerably smaller portion of their  
38 overall sunlit time at high SZA (e.g., between  $\sim 85$  and  $94^\circ$ )  
39 than is found for the January trajectories.

### 40 **4. Discussion**

41 We turn our attention to speculation regarding the cause of  
42 the rapid ozone loss during January. Standard photochemical  
43 models predict relatively slow rates of polar  $\text{O}_3$  loss at high  
44 SZA (e.g., between  $85$  and  $94^\circ$ ) because strong attenuation of  
45 UV light, due to the high  $\text{O}_3$  slant columns, limits the  
46 photolysis rate of  $\text{ClOOCl}$  and hence the overall rate of  $\text{O}_3$  loss  
47 by the  $\text{ClO}+\text{ClO}$  and  $\text{BrO}+\text{ClO}$  cycles.

48 Prior to the SOLVE/THESEO 2000 field campaign, we had  
49 speculated that photolysis of  $\text{ClOOCl}$  by an unknown state in  
50 the near IR (wavelengths  $> 800$  nm, which is optically thin  
51 even at high SZA) might provide a strong enhancement to the  
52 abundance of Cl and ClO during twilight. Such photolysis  
53 could lead to significant increases in chemical ozone loss rates  
54 at high SZA. Little change would occur for calculated loss

1 along trajectories in late February and early March because air  
2 parcels spend a much smaller fraction of overall sunlit time at  
3 high SZA. However, in-situ observations of ClO and ClOOCl,  
4 obtained from the NASA ER-2 during SOLVE, provide  
5 evidence that ClOOCl does not photolyze at an appreciable  
6 rate in the near IR [R. M. Stimpfle, private communication,  
7 2002]. Hence, we are left to ponder other possible causes of  
8 the observed rapid loss of ozone during January.

9 It is possible that O<sub>3</sub> is lost by reactions on the surface of  
10 PSCs (polar stratospheric clouds). The upper limit for the  
11 reaction probability of this process,  $2.5 \times 10^{-4}$  on the surface of  
12 nitric acid trihydrate [Sander *et al.*, 2000], suggests that this  
13 process could contribute significantly to ozone loss in January.  
14 For each January considered here, air was exposed to  
15 considerable amounts of PSCs during both day and night. Our  
16 finding that loss of ozone occurs only during sunlit periods  
17 suggests that, if direct loss on PSC surfaces is responsible,  
18 such loss must be driven by photons.

19 Observations indicate that BrO does not fall off with  
20 increasing SZA near sunset as rapidly as expected [Wahner  
21 and Schiller, 1992; Avallone and Toohey, 2001]. It is difficult  
22 to reconcile these observations with existing photochemical  
23 theory. Nonetheless, it is not clear how enhanced BrO in  
24 twilight could lead to appreciable increases in chemical loss  
25 rates since ClO is observed to decline with increasing SZA  
26 essentially as expected [Kreher *et al.*, 2002; R. M. Stimpfle,  
27 private communication, 2002]. A reactive partner is required  
28 for the enhanced levels of BrO, since the self-reaction of BrO  
29 is too slow to contribute appreciable amounts of ozone loss.  
30 Perhaps loosely bound higher oxides of ClOOCl contribute to  
31 the rapid ozone loss found in January, either by reaction with  
32 BrO or in other yet unidentified ozone loss cycles [Sander *et al.*,  
33 1989]. Better understanding of the photochemistry of this  
34 time period requires observations at high SZA, and appropriate  
35 potential temperature levels (e.g., 480 to 520 K), of BrO, other  
36 radicals, and a variety of chlorine species to test the budget and  
37 partitioning of halogens in the stratosphere.

## 38 5. Concluding Remarks

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

51 During cold Arctic Januaries we find cumulative ozone loss  
52 of about 0.5 ppmv. Although our and other analyses point  
53 toward the existence of a currently unknown ozone loss  
54 mechanism, its relative impact is modest for winters with  
55 massive ozone depletion. For such winters, loss of ozone  
56 predominantly occurs during February and March by known  
57 catalytic processes (ClO+ClO and ClO+BrO) that operate

1 efficiently under conditions of high solar illumination.  
 2 Nonetheless, the January discrepancy demands further  
 3 investigation because reliable assessments of future Arctic  
 4 ozone depletion require a full understanding of all significant  
 5 processes that affect ozone.

6  
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 15 project AFO 2000 / 07ATC08.

## 16 Notes

17 1. Values of BrO are found by specifying the sum, BrO+BrCl, as a  
 18 function of potential temperature such that observed mixing ratios of  
 19 BrO in the Arctic vortex [Harder *et al.*, 1998] are reproduced.  
 20 Measurements of O<sub>3</sub> from Match are also specified along each  
 21 trajectory.

22  
 23 2. Use of the Bloss *et al.* (2001) rate for ClO+ClO+M rather than the  
 24 JPL00-3 [Sander *et al.*, 2000] rate has essentially no effect on our  
 25 model calculations because a faster rate titrates ClO into ClOOCl.  
 26 Hence, the increase in O<sub>3</sub> loss due to the ClO+ClO cycle is nearly  
 27 balanced by the calculated decrease due to the BrO+ClO cycle.

28  
 29 3. An analysis of the individual errors of the Match events shows that  
 30 the distribution of errors is Gaussian [Rex, 1993]. However, based  
 31 on the sample size, it is hard to exclude a small, non-Gaussian  
 32 component at the far edge (e.g., beyond 2 $\sigma$ ) of the distribution. Since  
 33 faster than expected ozone loss rates are observed for all cold  
 34 Januaries, it is unlikely that the discrepancy discussed in this paper is  
 35 due to a statistical fluctuation of the data.

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41  
 42  
 43 Figure 1. Chemical loss rate of O<sub>3</sub> (O<sub>3</sub> *loss\_obs*) in the Arctic  
 44 vortex for indicated years and isentropic surfaces based on the  
 45 Match method (red boxes; error bars represent 1σ uncertainty).  
 46 The abundance of ClO<sub>x</sub> necessary to account for O<sub>3</sub> *loss\_obs*  
 47 along each trajectory (green dots; see text) for JPL00-3  
 48 kinetics is also shown. Also shown is an estimate of O<sub>3</sub> *loss\_mdl*  
 49 for January of each year assuming ClO<sub>x</sub>=3.7 ppbv (blue dashed  
 50 line).

51  
 52 Figure 2. Rate of change of ozone along Match trajectories for  
 53 data collected during sunlit conditions (defined as SZA < 95°)  
 54 and during dark periods (SZA > 95°) based on bivariate  
 55 regressions for data collected between 5 and 31 January of  
 56 each year for the set of matches used in Fig. 1. Error bars are  
 57 1σ estimates of the statistical uncertainty. During January 1996  
 58 a much smaller number of ozone soundings have been  
 59 performed compared to the other years shown here and the  
 60 uncertainty of the bivariate analysis is much larger.

61  
 62 Figure 3. Accumulated chemical loss of O<sub>3</sub> versus potential  
 63 temperature for Januaries of 1992 (black), 1995 (red), 1996  
 64 (green), and 2000 (blue). Results from Match analyses are  
 65 shown by solid lines with solid markers. The single open  
 66 marker represents a result from MLS for 1 to 31 January 1995  
 67 [Harris *et al.*, 2002]. The dotted lines represent ozone losses  
 68 derived from POAM II and III measurements. For these an  
 69 ozone versus PV relation was derived from POAM

1 measurements made during day  $32 \pm 2$  days. The vortex  
2 average ozone profile was calculated based on these relations  
3 at various heights. The ozone loss was then estimated by  
4 comparing this profile with subsided vortex average profiles  
5 calculated with the same approach for day  $5 \pm 2$  days. Error  
6 bars represent  $1\sigma$  uncertainties.

7  
8 Fig. 4. The chemical loss of  $O_3$  measured by Match between  
9 20 February 1996 and 3 March 1996 at 475 K versus the  
10 amount of sunlight exposure along each Match trajectory (red  
11 squares) and the computed reduction in  $O_3$  along the same  
12 Match trajectory based on MLS Version 5 measurements of  
13 ClO (green crosses). Error bars represent the  $1\sigma$  sigma  
14 standard deviation of the measured and modeled changes in  
15  $O_3$ .  
16

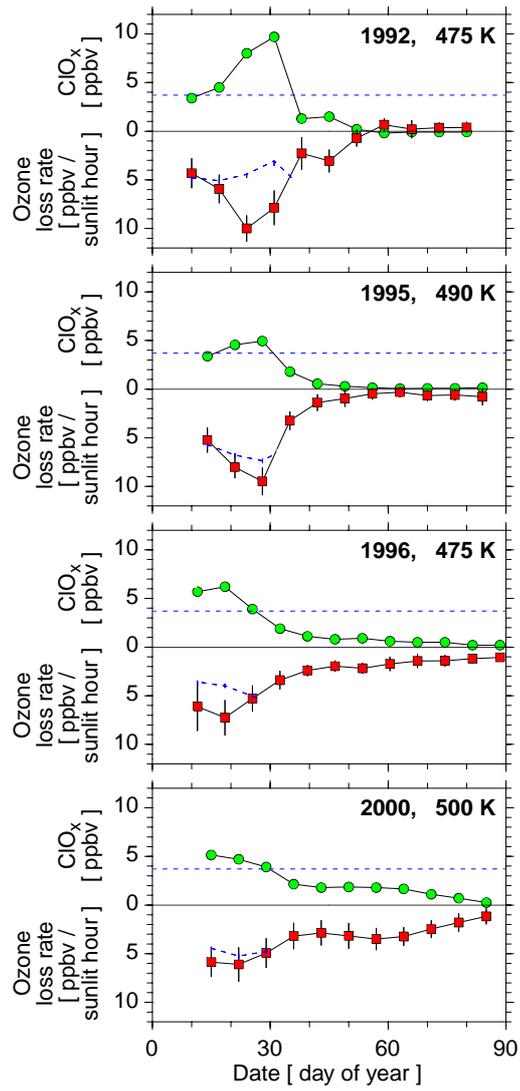


Figure 1, Rex et al.

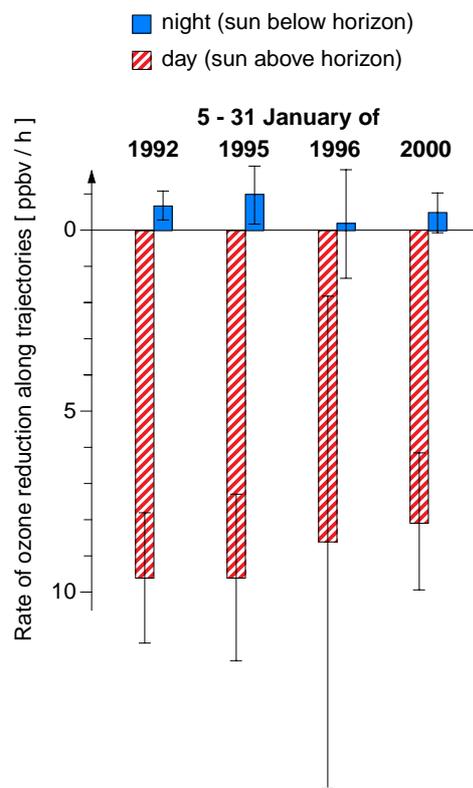


Figure 2, Rex et al.

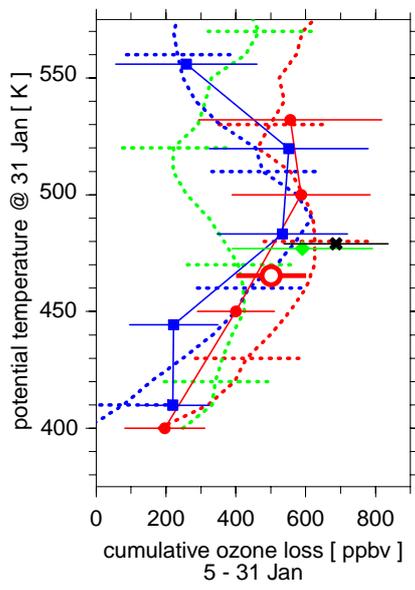


Figure 3, Rex et al.

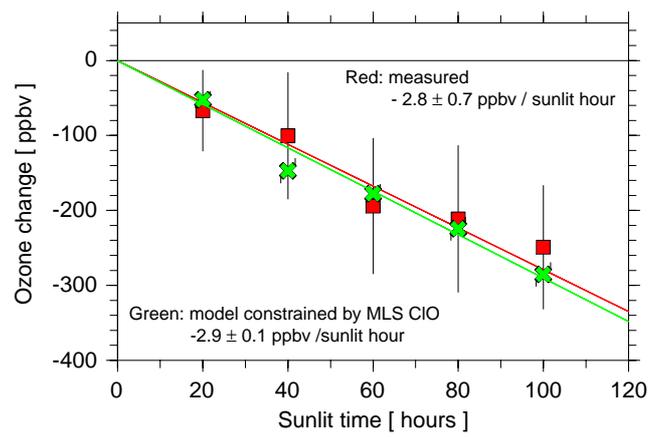


Figure 4, Rex et al.