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## Bromine-chlorine coupling in the Antarctic ozone hole

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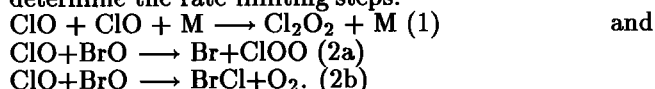
**Abstract.** The contribution from the chlorine and bromine species in the formation of the Antarctic ozone hole is evaluated. Since chlorine and bromine compounds are of different industrial origin, it is desirable, from a policy point of view, to be able to attribute chlorine-catalyzed loss of ozone with those reactions directly involving chlorine species, and likewise for bromine-catalyzed loss. In the stratosphere, however, most of the chemical families are highly coupled, and, for example, changes in the chlorine abundance will alter the partitioning in other families and thus the rate of ozone loss. This modeling study examines formation of the Antarctic ozone hole for a wide range of bromine concentrations (5 - 25 pptv) and for chlorine concentrations typical of the last two decades (1.5, 2.5 and 3.5 ppbv). We follow the photochemical evolution of a single parcel of air, typical of the inner Antarctic vortex (50 mbar, 70°S,  $\text{NO}_y = 2$  ppbv, with polar stratospheric clouds (PSC)) from August 1 to November 1. For all of these ranges of chlorine and bromine loading, we would predict a substantial ozone hole (local depletion greater than 90%) within the denitrified, PSC-perturbed vortex. The contributions of the different catalytic cycles responsible for ozone loss are tabulated. The deep minimum in ozone is driven primarily by the chlorine abundance. As bromine levels decrease, the magnitude of the chlorine-catalyzed ozone loss increases to take up the slack. This is because bromine suppresses ClO by accelerating the conversion of ClO and  $\text{Cl}_2\text{O}_2$  back to HCl. For this range of conditions, the local relative efficiency of ozone destruction per bromine atom to that per chlorine atom ( $\alpha$ -factor) ranges from 33 to 55, decreasing with increase of bromine.

### Introduction

The photochemical ozone balance in the stratosphere is governed by complex interactions between hydrogen, oxygen, nitrogen, chlorine and bromine species [WMO, 1992, 1995]. Discovery of the rapid ozone depletion under winter/spring conditions in Antarctica [Farman et al., 1985] stimulated several polar campaigns, where field measurements and model simulations were combined to explain this phenomenon (special issues of *Geophys. Res. Lett.*, 1986, vol.13, no.13; 1990, vol.17, no.4; *J. Geophys. Res.*, 1989, vol. 94, nos. D9 and D14; 1992, vol.97, no.D8; *Science*, 1993, vol.261, p.1128-1158). These and subsequent work identified the three chemical mechanisms, unknown at the time of Farman's discovery, that are all essential to formation of the ozone hole: (1) activation of chlorine compounds on PSCs

[Solomon et al., 1986]; (2) the ClO-ClO catalytic cycle for ozone loss [Molina and Molina, 1987]; and (3) the denitrification of the central vortex [Fahey et al., 1990]. The previously identified ClO-BrO catalytic cycle [Clyne and Watson, 1977; Yung et al., 1980] was also suggested to play an important role in formation of the ozone hole [McElroy et al., 1986].

For conditions typical during formation of the ozone hole, there are two predominant catalytic cycles that determine the rate limiting steps:



In addition to (2a,b) BrO also reacts with ClO via  $\text{ClO} + \text{BrO} \longrightarrow \text{Br} + \text{OClO}$  (2c). Reactions (2a,b,c) defines the coupling between bromine and chlorine species. Analysis of the aircraft measurements by Anderson et al. [1989] attributes 16-28% of the total ozone loss to reactions 2a,b (their Fig.24). Similar estimates obtained by Ko et al. [1989], Solomon et al. [1990], and Sanders et al. [1993] are valid for recent levels of chlorine and bromine in the stratosphere.

Current international protocols have agreed on phase-out of CFCs, HCFCs and halons. Future control of  $\text{CH}_3\text{Br}$  used as a soil and crop fumigant is under consideration. The goal of this note is to investigate how a proposed reduction of bromine loading might affect the Antarctic ozone hole. We focus on the partitioning of the chlorine species and the ozone balance in the denitrified polar lower stratosphere. Such polar ozone loss is of interest not only for the hole, but also because it drives some of the mid-latitude loss in the southern hemisphere [Sze et al., 1989, Prather et al., 1990]. We also evaluate a value of the parameter  $\alpha_{local}$  defined as the local efficiency of a bromine atom in the catalytic removal of ozone relative to that of a chlorine atom.

### Description of Calculation

Modeling of the complete evolution of the Antarctic ozone hole is exceedingly difficult, because the formation of the inner, denitrified region is not easy to predict. Nevertheless, once the denitrified region is formed, the uniformity of PSC processing [Manney and Zurek, 1993], the lack of strong mixing within this quasi-homogeneous inner chemical vortex [Schoeberl and Hartmann, 1991], and the existence of a stable polar vortex usually until the beginning of November [Santee et al., 1995], allow us to treat the evolution of the ozone in the vortex with a simple, photochemical box model. We follow the photochemical evolution of an isolated air parcel fixed at 70°S and 50 mbar for 100 days beginning August 1. Observations [Santee et al., 1995] show that this point is well inside the polar vortex and almost completely denitrified.

The photochemical calculations are carried out using a box-model version of the photochemical module in the

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**Table 1.** Heterogeneous Reactions and Its Reaction Probabilities on/in Sulfate Aerosol and type I PSCs

Reaction	aerosol	PSC I
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	0.1 <sup>a</sup>	0.0003 <sup>a</sup>
$\text{N}_2\text{O}_5 + \text{HCl} \rightarrow \text{ClNO}_2 + \text{HNO}_3$	-	0.003 <sup>a</sup>
$\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$	$\gamma_2^b$	$f(\text{RH})^d$
$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$	$\gamma_3^b$	0.001 <sup>a</sup>
$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$	bulk <sup>a</sup>	0.1 <sup>a</sup>
$\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HNO}_3$	0.4 <sup>c</sup>	-
$\text{HOBr} + \text{HCl} \rightarrow \text{BrCl} + \text{H}_2\text{O}$	bulk <sup>c</sup>	-

<sup>a</sup>DeMore et al.,1994; <sup>b</sup>Hanson and Ravishankara,1994;

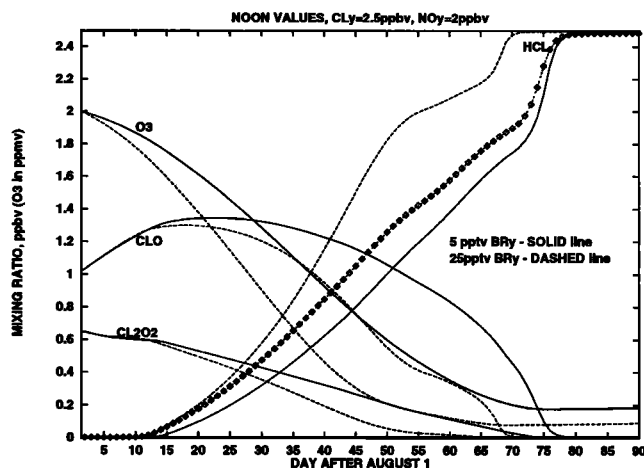
<sup>c</sup>Hanson and Ravishankara,1995; <sup>d</sup>function of relative humidity (<0.23) by Hanson and Ravishankara, 1993

AER 2-D model [Weissenstein et al., 1993] to which we have added the species BrCl, ClNO<sub>2</sub>, and HONO. Gas-phase reaction constants and cross sections are taken from DeMore et al. [1994], except for the cross sections of HOBr [Orlando and Burkholder, 1995] and BrONO<sub>2</sub> [Burkholder et al., 1995]. Photolysis rates are calculated at each time step (30 minutes), taking into account spherical geometry at low sun [Prather and Remsberg, 1993, p.76-85]. The heterogeneous reactions on/in sulfate aerosol and on type I PSCs are given in Table 1 and use recommendations of DeMore et al. [1994] and Hanson and Ravishankara [1993, 1994, 1995] in the manner described in Danilin and McConnell [1994, 1995]. We include only two bromine heterogeneous reactions on/in sulfate aerosol BrONO<sub>2</sub> + H<sub>2</sub>O → HOBr + HNO<sub>3</sub> and HOBr + HCl → BrCl + H<sub>2</sub>O [Danilin and McConnell, 1995] and adopt a time-invariant sulfate aerosol surface area equal to 0.6 μm<sup>2</sup>/cm<sup>3</sup> with particle radius of 0.1 μm. The SAM II analysis indicates occurrence of PSC until November [Poole and Pitts, 1994; Fig.2]. We prescribed the temperature in our model to produce continuous PSC processing from the starting day (August 1) until October 6.

The model is initialized with very low values of total odd-nitrogen, NO<sub>y</sub>=2 ppbv, typical of the Antarctic ozone hole and consistent with UARS data and the in situ measurements of Fahey et al [1989]. The initial contents of the long-lived species are equal to 2 ppmv of O<sub>3</sub>, 4.5 ppmv of H<sub>2</sub>O, 0.5 ppmv of H<sub>2</sub>, and 1.2 ppmv of CH<sub>4</sub> [Heidt et al, 1989]. We present results for total bromine Br<sub>y</sub> (=Br+ BrO+ HOBr+ BrONO<sub>2</sub>+ HBr+ BrCl) ranging from 5 to 25 pptv and total chlorine Cl<sub>y</sub> (=Cl +ClO +HOCl +HCl+ ClONO<sub>2</sub>+ ClNO<sub>2</sub> +OCIO +BrCl+2×(Cl<sub>2</sub>O<sub>2</sub>+Cl<sub>2</sub>)) levels of 1.5, 2.5, and 3.5ppbv.

## Results and Discussion

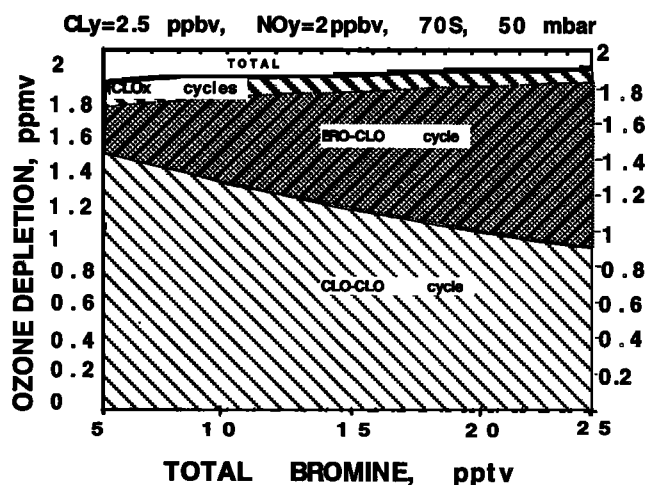
Bromine loading influences both the depth of the ozone loss and the duration of high ClO concentrations. Figure 1 shows the August-October history of noontime concentrations of O<sub>3</sub>, ClO, Cl<sub>2</sub>O<sub>2</sub>, and HCl for 5 pptv (solid lines) and 25 pptv (dashed lines) of Br<sub>y</sub> with 2.5 ppbv of Cl<sub>y</sub>. Increase of Br<sub>y</sub> from 5 to 25 pptv leads to faster and deeper (91 and 96% respectively in the middle of October) ozone depletion. ClO reaches its maximum of almost 1.4 ppbv in August (consistent with the MLS observations reported by Santee et al. [1995]) and falls below 0.02 ppbv in October. Cl<sub>2</sub>O<sub>2</sub> behaves similarly with a maximum noon value near 0.6 ppbv in the beginning of August, when the solar zenith angle is larger than 87°. This figure shows that model calculates higher ClO concentration and slower HCl recovery for lower bromine loadings.



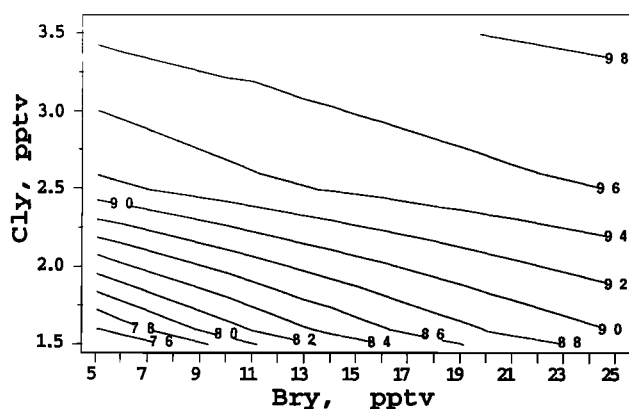
**Figure 1.** Temporal behavior of the noon values of ozone, ClO, Cl<sub>2</sub>O<sub>2</sub>, and HCl for 5 (solid line) and 25 pptv (dashed line) of Br<sub>y</sub> after August 1 at 70°S, 50 mbar level Cl<sub>y</sub>=2.5 ppbv, and NO<sub>y</sub>=2 ppbv. Dashed line with symbols depicts the evolution of HCl calculated for 25 pptv of Br<sub>y</sub>, but with O<sub>3</sub> taken from the Br<sub>y</sub>=5 pptv case. See text for discussion.

HCl recovery becomes significant in September and the HCl concentration increases rapidly to ~2.5 ppbv as O<sub>3</sub> is depleted [Prather and Jaffe, 1990]. Compared to the case with Br<sub>y</sub>=25 pptv, the conversion of the chlorine radicals to the unreactive HCl is delayed by about 10-20 days for the Br<sub>y</sub>=5 pptv case. This is because of the coupling of the two families through reactions (2a,b), which are the main process for converting ClO to Cl in the denitrified lower stratosphere. To separate the effects of ozone and bromine loading on the rate of the HCl recovery, we made a run for Br<sub>y</sub>=25 pptv, but with the O<sub>3</sub> prescribed at that calculated for Br<sub>y</sub>=5 pptv. Dashed line with symbols shows that the rate of the HCl recovery depends primarily on the difference in Br<sub>y</sub> in August and on the difference in ozone concentration in late September-October.

This coupling of the Br<sub>y</sub> and Cl<sub>y</sub> families means that changes in Br<sub>y</sub> alter the partitioning between active and



**Figure 2.** Cumulative ozone loss (in ppmv) between August 1 and the day of maximum ozone depletion by the main catalytical cycles as a function of bromine loading of the stratosphere for Cl<sub>y</sub>=2.5 ppbv.



**Figure 3.** Maximum ozone depletion (in % of the initial ozone value of 2 ppmv) at 50 mbar and 70°S as a function of chlorine and bromine loadings. These values correspond to the continuous PSC processing until October 6 and  $\text{NO}_y=2$  pptv.

passive chlorine and affect the ozone loss rates. Figure 2 shows the contribution of the ClO-ClO cycle (bottom area), the ClO-BrO cycle (middle area) and all other ClO<sub>x</sub> cycles (top area) to the total ozone loss from August 1 to the day of the maximum O<sub>3</sub> depletion as a function of Br<sub>y</sub>. Ozone loss from other bromine cycles (e.g., BrO+O and BrO+HO<sub>2</sub>) and other families (e.g., HO<sub>x</sub> and NO<sub>x</sub>) are insignificant. The decreasing importance of the ClO-BrO cycle in ozone depletion for lower Br<sub>y</sub> is offset for the most part by the rise in loss driven by the ClO-ClO cycle. Although up to 50% of the ozone loss can be attributed to bromine catalytic cycles at 25 pptv of Br<sub>y</sub>, a reduction of bromine levels would not “repair” the ozone hole at anywhere near this proportion.

Indeed, it is the amount of Cl<sub>y</sub> that primarily determines the depth of the ozone depletion. In Figure 3 we plot the maximum ozone loss (in % of the initial value of 2 ppmv) as a function of Br<sub>y</sub> for the levels of Cl<sub>y</sub> in the Antarctic stratosphere changing from 1.5 pptv (typical of the early 1970s before the clear identification of the Antarctic ozone hole) via 2.5 pptv (typical of the 1980s when the ozone hole was a regular feature) to 3.5 pptv (expected maximal loading in this decade as CFC levels decline in response to the Montreal Protocol and its amendments). It is clear that chlorine levels control the maximal ozone depletion within the Antarctic ozone hole, and it is only at the current levels, in excess of 3 pptv, that we can achieve local ozone loss greater than 95% as observed in the past few years [Hofmann et al., 1993].

In recent ozone assessments [WMO, 1992;1995] the importance of bromine-catalyzed loss relative to chlorine-catalyzed loss (on an atom-per-atom basis) has been denoted by the parameter  $\alpha$ . This  $\alpha$  is formally defined as an averaged quantity for global ozone loss (i.e., all latitudes, all seasons, and all heights) and currently is computed by two-dimensional stratospheric chemical models assuming a given level of chlorine and bromine. As we have just shown above, the coupling of the different chemical families means that diagnostic attribution of ozone loss to catalytic cycles cannot be used to predict changes in O<sub>3</sub> if the Cl<sub>y</sub>, Br<sub>y</sub>, NO<sub>y</sub> and HO<sub>y</sub> loading and radical partitioning are expected to change [Wennberg et al., 1994].

We examine the parameter  $\alpha_{local}$  defined to reflect ozone loss typical of the core of the Antarctic ozone

hole. The formal definition is

$$\alpha_{local} = \frac{\partial \Delta O_3 / \partial Br_y}{\partial \Delta O_3 / \partial Cl_y} \quad (1)$$

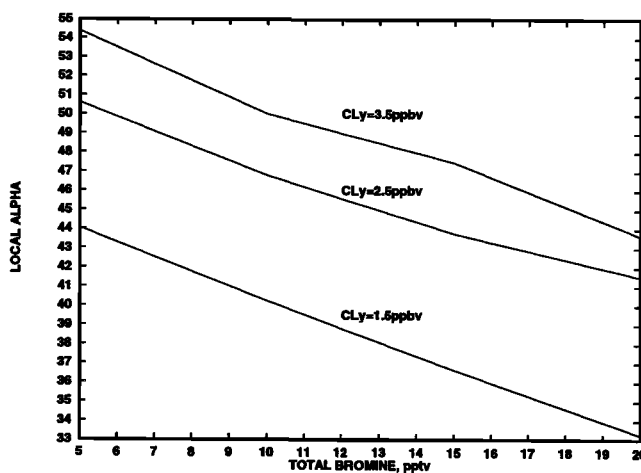
where  $\Delta O_3$  is the difference between maximum ozone depletions for the two consecutive levels of Br<sub>y</sub> or Cl<sub>y</sub> and the partial derivatives are evaluated numerically by perturbing only Br<sub>y</sub> or Cl<sub>y</sub> by 1 pptv and 0.1 ppbv, respectively. The resulting values of  $\alpha_{local}$ , applicable only to the Antarctic ozone hole, are shown in Figure 4. Its values are between 33 to 55 and coincidentally include the usually quoted global values of 40-50 [WMO, 1992; 1995].

We also looked at the other latitudes (65°S) and the different extent of the denitrification (0.1 and 1 ppbv of NO<sub>y</sub>). Latitudinal dependence in the polar vortex is not important provided the same conditions of denitrification and PSC processing apply, only the timing of maximum ozone depletion changes. More extreme denitrification, 0.1 to 1 ppbv NO<sub>y</sub>, results in larger cumulative ozone depletion as expected since less active ClO can be tied up in ClONO<sub>2</sub>. Effects of bromine loading on the ozone balance at mid-latitudes and tropics requires additional analysis, taking into account the effect of transport and coupling of different bromine, chlorine, nitrogen and hydrogen cycles as affected by variable aerosol loading, temperature and solar angles.

## Summary

Our results are valid inside Antarctic winter-spring vortex and demonstrate the necessity of taking into account the coupling of different families, specifically chlorine and bromine, in studying the recovery of the ozone layer in the atmosphere or evaluating the ODP of the anthropogenic species [Fisher et al., 1990; Solomon et al., 1992; WMO, 1992]. Reduction of the bromine loading could change partitioning of chlorine in favor of its active forms (ClO, Cl<sub>2</sub>O<sub>2</sub>), thus compensating the expected ozone recovery.

The chlorine-bromine coupling in the lower Antarctic stratosphere makes it difficult to diagnose changes in ozone depletion by scaling the catalytic cycles alone, without accounting for correlated changes in partitioning. The two- and three-dimensional models used in assessments already account for this if they calculate



**Figure 4.**  $\alpha_{local}$  as a function of bromine loading for 1.5, 2.5 and 3.5 pptv of Cl<sub>y</sub>.

the sensitivity to bromine by changing  $Br_y$  through the abundance of  $CH_3Br$  or the halons, but not if they merely scale the catalytic cycles in proportion to bromine. Equally important, the recovery of the ozone hole cannot be diagnosed merely from the measured abundances and the inferred rate-limiting catalytic cycles. Our calculations indicate that the  $\alpha_{local}$  in the Antarctic region is dependent on the assumed background levels of  $Cl_y$  and  $Br_y$ . This fact should be considered in regulatory use of  $\alpha$  and ODP values for brominated compounds. Further analysis with the global chemical models in conjunction with measurements is needed to quantify the relative roles of bromine and chlorine for the ozone depletion observed in all seasons, at mid-latitudes, and in the Arctic winter [Stolarski et al., 1992], especially if we are to attribute recovery of ozone depletion to specific reductions in anthropogenic chlorine or bromine compounds.

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