

The importance of heterogeneous bromine chemistry in the lower stratosphere

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Abstract. Heterogeneous conversion of bromine reservoirs (BrONO₂, HOBr) on the surface of aerosol particles in the lower stratosphere has limited effect on the concentrations of reactive bromine radicals (Br, BrO). However, the heterogeneous hydrolysis of BrONO₂ on sulfate aerosol particles, which produces HOBr, leads to the enhancement of the abundance of hydroxyl radicals, and consequently modifies the partitioning between inorganic chlorine compounds. Further, because of the enhanced abundance of HOBr, the heterogeneous reaction between HOBr and HCl(s) converts significant amounts of inactive chlorine (HCl) into reactive chlorine (ClO), especially during post-volcanic periods. These processes could partially explain the unexpected high ClO/HCl and ClONO₂/HCl concentration ratios at 20 km reported after the eruption of Mt. Pinatubo (1991), and could have contributed to the substantial ozone depletion observed after the large volcanic eruptions of the 1980's and 1990's. Our model simulations suggest that, owing to the heterogeneous hydrolysis of BrONO₂ and the reaction HOBr+HCl(s) on sulfate aerosols, the increase in total bromine loading from 1960 (12 pptv) to 1990 (21 pptv) has led to enhanced concentrations of ClO, and consequently to an ozone depletion of 2-3% in the lower stratosphere at mid- and high latitudes under post-volcanic conditions.

Introduction

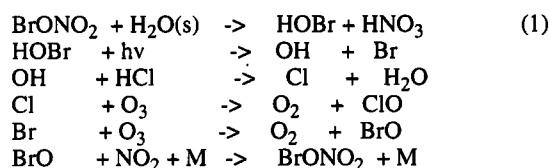
In spite of its low abundance [10-20 pptv, see WMO, 1992], bromine plays an important role in the lower stratosphere [Yung et al., 1980; McElroy et al., 1986; Poulet et al., 1992; Garcia and Solomon, 1994; Danilin and McConnell, 1995; Hanson and Ravishankara, 1995; Lary, 1995; Lary et al., 1995]. The major source of reactive bromine (Br, BrO) above the tropopause is provided by the photolysis and oxidation of organic bromine molecules such as methyl bromide (emitted at the surface by natural and anthropogenic processes, Singh et al., [1993]). Industrially manufactured halons (H-1211, H-1301, etc.) contribute approximately 50% of the inorganic bromine in the stratosphere [Schauffler et al., 1993].

While the effects of chlorine on the ozone depletion have been extensively studied [WMO, 1992], the role of bromine in the chemistry of the lower stratosphere is less well understood. The purpose of this paper is to assess the importance of bromine for the chemistry of the stratosphere, and especially to estimate how the heterogeneous conversion of BrONO₂ and HOBr during post-volcanic periods affects the partitioning between the members of other chemical families. The direct and indirect influences of bromine on stratospheric ozone will also be considered

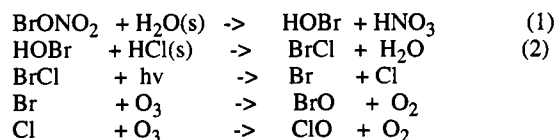
Modeling of the Effects of Bromine

In the presence of sulfate aerosols, bromine nitrate (BrONO₂) is rapidly converted into HOBr [Hanson and Ravishankara,

1995], which photolyzes to produce hydroxyl radicals (OH) [Hanson et al., 1996]. The sequence which leads to the conversion of inactive chlorine (HCl) to reactive chlorine (ClO) is the following [Danilin and McConnell, 1995; Lary et al., 1995; Hanson and Ravishankara, 1995] (sequence A):



where (s) stands for molecules in the condensed phase. As a result of the OH production, the concentration of HCl is reduced in favor of reactive chlorine (Cl, ClO), which leads to enhanced ozone destruction. As ClO reacts rapidly with NO₂, the density of ClONO₂ is also increased and that of NO_x decreased. These effects are reinforced by the heterogeneous reaction of gas-phase HOBr with HCl molecules condensed inside the aerosol droplets, through the following reaction sequence (sequence B)



The accommodation coefficient for the BrONO₂ heterogeneous hydrolysis is believed to be only weakly dependent on the weight percentage of the sulfuric acid in the aerosol [Hanson and Ravishankara, 1995], and in the model is set to 0.4 at all temperatures. The corresponding coefficient for reaction (2) varies strongly with aerosol composition. Since the solubility of HOBr is approximately 10 times larger than that of HOCl in sulfate particles [Hanson and Ravishankara, 1995] and the rate for reaction of HOBr with HCl is approximately the same as for HOCl with HCl [Abbott, 1994; Hanson and Ravishankara, 1995], the uptake coefficient for reaction (2) is set to be 10 times larger than that of the HOCl + HCl(s) reaction, with an upper limit of unity [Hanson, et al., 1994]. More laboratory measurements are needed to better qualify this reaction coefficient.

In order to quantify the importance of bromine for the chemistry of the lower stratosphere, we use the three-dimensional (3-D) chemical transport model described by Brasseur et al. [1996], but with a spatial resolution of 5.6 degrees in latitude and 11.2 degrees in longitude, and with 44 levels in the vertical (from the surface to the altitude of 80 km). The transport, which is formulated by the semi-Lagrangian scheme of Williamson and Rasch [1989], is driven by winds provided by the stratospheric version of the NCAR Community Climate Model. The calculated temperature is consistent with National Meteorological Center data analyses [Boville, 1995]. The chemical scheme (46 species with 137 chemical and photochemical reactions with rate constants taken from DeMore et al., 1994). Key heterogeneous reactions (aerosols and polar stratospheric clouds) are taken into account. Aerosol surface areas representative of non-volcanic periods (background conditions) are based on observations by SAGE [WMO, 1992].

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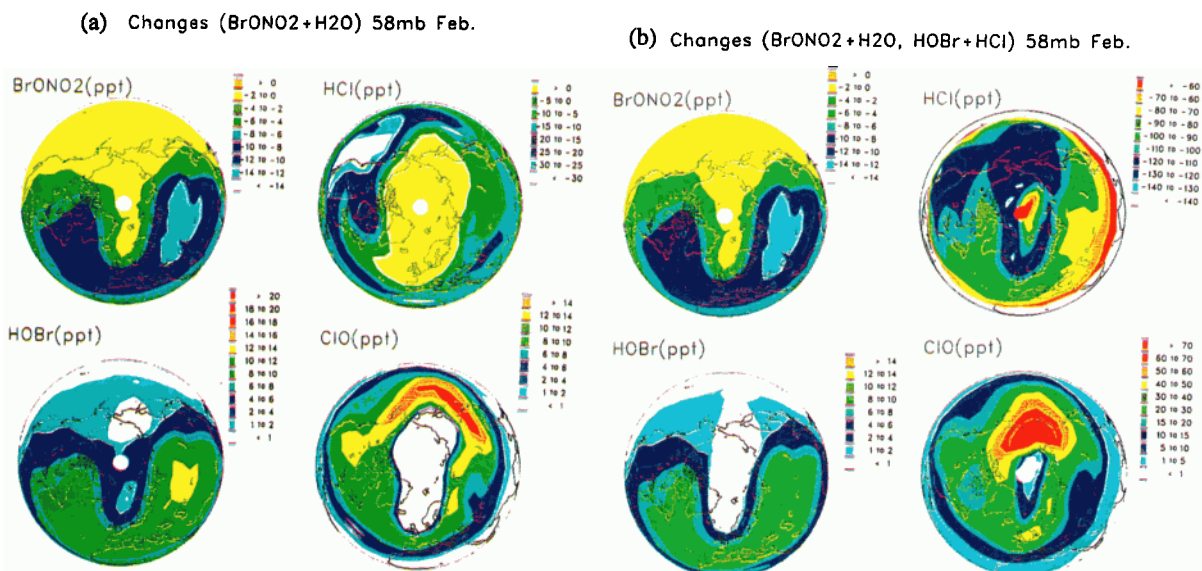


Figure 1, Calculated changes (pptv) in BrONO₂, HOBr, HCl, and ClO at 58 mb in February at zero UT (a) resulting from the introduction of the BrONO₂ heterogeneous hydrolysis, and (b) with combined the BrONO₂+H₂O(s) and HOBr+HCl(s) reactions.

For post-volcanic conditions, we make the simple assumption that background values are multiplied by a factor of 20. The reactions of bromine species on the surface of water ice (type II PSCs) are ignored in the model. The chemical transport equations are solved by a splitting operator technique; at each timestep, the mixing ratios of the chemical species are successively updated in the following order: (1) advection by the semi-Lagrangian technique, (2) chemical transformations, (3) mixing accounting for vertical subgrid transport, and (4) redistribution by convection. The model is integrated over a period of one year. Initial conditions for the concentration of chemical compounds are representative of June, and are taken from zonally averaged concentrations provided by our 2-D model [Brasseur et al., 1990; Granier and Brasseur, 1993].

As indicated above, both reactions sequences (A) and (B) convert inactive chlorine (HCl) to reactive chlorine (ClO), and it is therefore important to quantify the contribution made individually by these processes. Figure 1a shows the changes in the concentrations of BrONO₂, HOBr, HCl, and ClO at 58 mb in February when only the heterogeneous hydrolysis of BrONO₂ (sequence A) is taken into account (post-volcanic conditions). The calculation shows that the concentration of BrONO₂ decreases by up to 12 ppt and that simultaneously, the concentration of HOBr increases by a maximum of 12 ppt during nighttime. Since the total bromine at this level is of the order of 15 pptv, it indicates that during the night the dominant bromine species, which is originally BrONO₂, becomes HOBr due to the heterogeneous hydrolysis of BrONO₂. During daytime, HOBr is rapidly photolyzed and produces OH. Through reaction with OH, the concentration of HCl decreases (by more than 30 ppt), while that of ClO increases (by more than 20 ppt). When sequence B is also taken into account, the calculated concentrations of HOBr and HCl decrease at high latitudes (see Figure 1b) where the temperature is low and the reaction coefficient of (2) is high. As a result, the concentration of ClO increases by up to 70 ppt at high latitudes during daytime. Comparing Figure 1a to Figure 1b, we note that the changes in the concentrations of HCl and ClO are higher in the case where both reaction sequences are taken into account. However, note that sequence B can not be important without reaction (1), which is necessary to provide the reactant (HOBr).

The total net effect of heterogeneous reactions (1) and (2) on the concentrations of chlorine compounds (HCl, ClONO₂, and

ClO) in February is shown in Figure 2 for post-volcanic conditions. As expected, the concentration of HCl in the lower stratosphere (20 km) is reduced by as much as 100-140 pptv at mid- and high latitudes (25% at the North Pole and 12% at 45 degrees). This decrease is compensated by an increase in the abundance of ClO (50 pptv, or 35% at high latitudes where the NO_x density is low) and of ClONO₂ (50 pptv or 8% at mid-latitudes where NO_x is available). For an aerosol load representative of background conditions (not shown), the impact of heterogeneous bromine reactions is significantly reduced: the decrease in the HCl density at 20 km is typically 20-30 pptv (or 2-3%) at high and mid-latitudes.

Since the effect of bromine is very sensitive to the surface area density available, the ClO/HCl and ClONO₂/HCl concentration ratios in the lower stratosphere change substantially with the aerosol load (see Table 1). For example, the calculated concen-

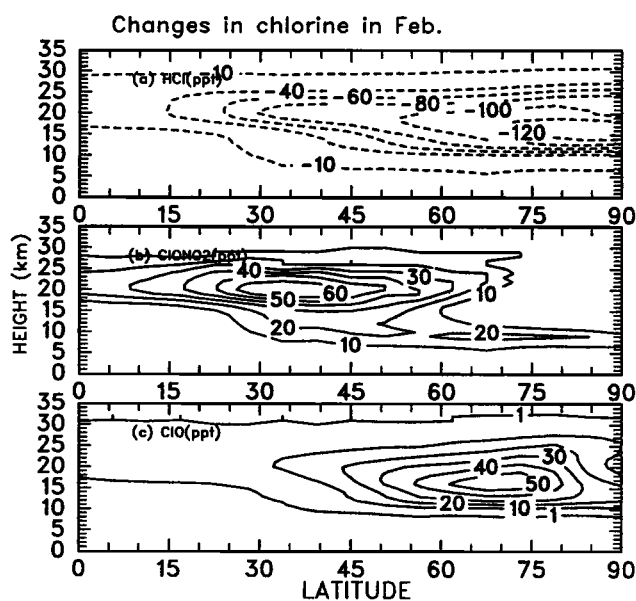


Figure 2, Calculated changes (pptv) in HCl (a), ClONO₂ (b), and ClO (c) in February due to the effects of heterogeneous reactions of bromine on the surface of post-volcanic aerosols.

Table 1. Chlorine partitioning at 70 mb in February with including the heterogeneous reactions of bromine taken into account.

	19N	30N	41N	52N	63N	74N	Obs.
<u>CIO/HCl</u>							
BG*	0.00	0.01	0.02	0.03	0.05	0.06	
VOL**	0.02	0.04	0.10	0.18	0.33	0.52	0.15 ⁽¹⁾
<u>HCl/Cly</u>							
BG*	0.79	0.66	0.58	0.55	0.52	0.49	(0.73 ± 0.1) ⁽³⁾
VOL**	0.66	0.51	0.41	0.36	0.31	0.24	0.40 ⁽²⁾
<u>CIONO₂/Cly</u>							
BG*	0.21	0.33	0.40	0.43	0.44	0.42	(0.27 ± 0.1) ⁽³⁾
VOL**	0.32	0.46	0.53	0.54	0.50	0.37	(0.45 ± 0.15) ⁽⁴⁾
<u>CIONO₂/HCl</u>							
BG*	0.26	0.51	0.70	0.78	0.85	0.86	
VOL**	0.48	0.91	1.30	1.48	1.62	1.57	

(1) Webster et al. (1993a), March, 1992, 26°N–42°N (airmass unperturbed by PSCs), daytime.

(2) Webster et al. (1993b), December, 1991–March, 1992, 22°N–69°N (airmass unperturbed by PSCs), daytime.

(3) Zander et al. (1990), April–May, 1985, 29°N, daytime.

(4) Dessler et al. (1995), February–March, 1993, 30°N–60°N, nighttime.

* BG = Background aerosol condition

** VOL = Post-volcanic aerosol condition

tration of ClO relative to that of HCl at 41°N and 70 mb is enhanced from 2% with background aerosol, to 10% in the case of volcanic aerosol, suggesting that heterogeneous reactions involving bromine compounds contribute significantly to the conversion of HCl to ClO during volcanic periods. However, we notice that the calculated ratio of ClO/HCl is approximately 35% smaller than the *in situ* observations (15% during volcanic period) of Webster et al. [1993a], indicating that additional mechanisms may play an important role. Under post-volcanic conditions, the calculated HCl accounts for approximately 41% of the odd chlorine family (Cly) at 41°N, and ClONO₂ for 53%. During non-volcanic periods, these contributions are 58 and 40%, respectively. The effect of heterogeneous reactions (1) and (2) could therefore account for the differences between recent *in situ* observations and earlier model calculations [see Webster et al., 1993a; 1993b]. It could partially explain why, according to the measurements of Webster et al. [1993b] (made after the eruption of Mt. Pinatubo), HCl accounts for only 40% of Cly near 20 km, while, based on the measurements made from the Shuttle during non-volcanic periods in the late 1980's [Zander et al., 1990], HCl was the dominant member of Cly family between 20 and 30 km. Correlated observations of HCl and ClONO₂ in 1992/1993 from two instruments (HALOE and CLAES) on board the Upper Atmosphere Research Satellite (UARS) suggest that total inorganic chlorine at low and mid-latitudes was evenly distributed between these two molecules in the lower stratosphere [Dessler et al., 1995]. The calculated concentration ratios of HCl/Cly and ClONO₂/Cly lie between the two sets of observations [Webster et al., 1993d; Dessler et al., 1995].

As the abundances of reactive chlorine and bromine radicals are enhanced through sequences A and B, the destruction of ozone is also enhanced. Figure 3 suggests that the change in the ozone destruction rate (expressed in ppmv/yr.) due to the two heterogeneous reactions (1) and (2) under volcanic conditions, occurs mainly through the chlorine catalytical cycle, rather than by the bromine catalytical cycle (the HOx cycle contributes to an additional 10%). Thus, the major effect of the heterogeneous bromine reactions is to amplify the ozone destruction by reactive chlorine. The reduction in the ozone concentration caused by reactions (1) and (2) in the model reaches 3.5% in the lower stratosphere at mid- and high latitudes. It is likely that these reactions, through this amplification mechanism, have contributed to the ozone depletion observed after the volcanic eruptions of El Chichon (1982) and Mt. Pinatubo (1991).

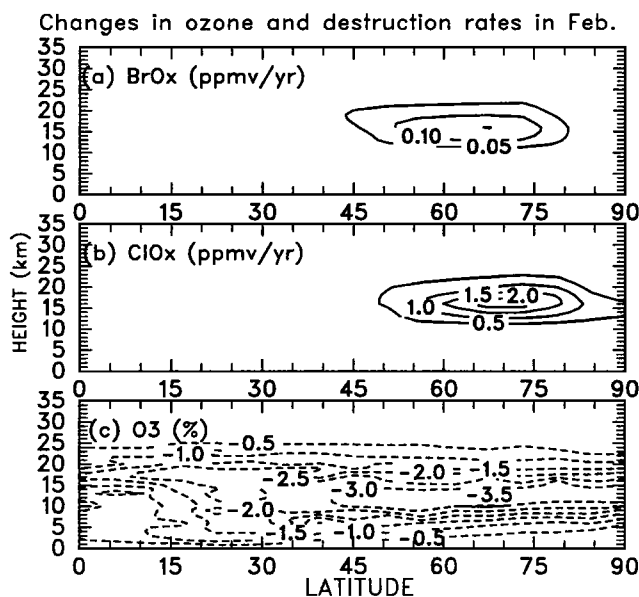


Figure 3. Calculated changes in the destruction rates of ozone (ppmv/year) by the BrOx catalytical cycle (a), and the ClOx catalytical cycle (b), as well as the relative change in the ozone concentration (%) (c) induced by the effects of heterogeneous reactions of bromine on the surface of post-volcanic aerosols. BrOx destruction reactions include BrO+BrO, BrO+ClO, as well as BrO+HO₂. ClOx destruction reactions include ClO+ClO, ClO+HO₂. Calculation refer to February condition. The ClO+O, and BrO+O reactions are ignored because their role in the lower stratosphere is insignificant.

Finally, we investigate the stratospheric impact of the growth in the bromine abundance which is believed to have occurred as a result of human activities. We assume that the mixing ratio of total inorganic bromine has increased from 12 pptv for total inorganic bromine species (a value representative of the 1960's) to 21 pptv (corresponding to 1990's). As shown by Figure 4, (for

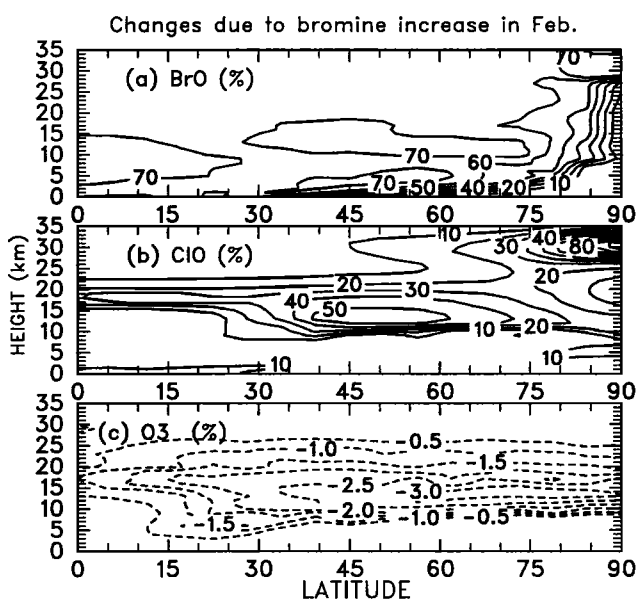


Figure 4. Calculated changes in the concentration of BrO (%) (a), ClO (%) (b), and O₃ (%) (c) in February to the temporal increase of inorganic bromine between 1960's and 1990's. The effects of heterogeneous reactions of bromine on the surface of post-volcanic aerosols are included in the calculation.

which post-volcanic aerosol loads are assumed), the increase in bromine causes an approximately 20 to 50% increase in the mixing ratio of ClO in the northern lower stratosphere in winter. Because the absolute concentrations of ClO are approximately 50 to 100 times larger than those of BrO at the same locations, the impact on ozone (primarily by the ClO+ClO reaction) of increasing bromine abundances is provided primarily by the change in the chlorine partitioning rather than by the changes in the abundance of BrO. The calculated reduction in the ozone concentration reaches 2-3% in the lower stratosphere at mid- and high latitudes (1-1.5% in the case of ozone column). This effect could account, at least in part, for the underestimation of the mid-latitude ozone depletion calculated after the eruption of Mt. Pinatubo and reported by Tie et al. [1994].

Conclusions

Model calculations made by our 3-D chemical transport model of the atmosphere suggest that bromine compounds play a considerable role in the contemporary lower stratosphere, particularly after larger volcanic eruptions. Both the heterogeneous hydrolysis of BrONO₂ and the reaction of HOBr+HCl(s) in sulfate aerosols play important roles in the conversion of inactive chlorine (HCl) into reactive chlorine (ClO). The heterogeneous hydrolysis of BrONO₂ followed by the photolysis of HOBr enhances the abundance of hydroxyl radical and, consequently, modifies the partitioning between inorganic chlorine compounds. Further, the heterogeneous reaction between HOBr and HCl(s) converts significant amount of HCl to ClO. As a result, the efficiency of the ozone destruction by stratospheric chlorine is amplified. Bromine could, therefore, have contributed indirectly to the ozone depletion observed at mid-latitudes in the 1980s and 1990s, especially during post-volcanic periods.

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