Surface ozone depletion in Arctic spring sustained by bromine reactions on aerosols

Song-Miao Fan & Daniel J. Jacob

Pierce Hall, 29 Oxford Street, Division of Applied Sciences,
Harvard University, Cambridge, Massachusetts 02138 USA

NEAR-TOTAL depletion of the ozone in surface air is often observed in the Arctic spring, coincident with high atmospheric concentrations of inorganic bromine[1-5]. Barrie *et al.*[1] suggested that the ozone depletion was due to a catalytic cycle involving the radicals Br and BrO (ref. 6); however, these species are rapidly converted to the nonradical species HBr, HOBr and $BrNO_3$, quenching ozone loss. McConnell *et al.*[7] proposed that cycling of inorganic bromine between aerosols and the gas phase could maintain sufficiently high levels of Br and BrO to destroy ozone, but they did not specify a mechanism for aerosol-phase production of active bromine species. Here we propose such a mechanism, based on known aqueous-phase chemistry, which rapidly converts HBr, HOBr and $BrNO_3$ back to Br and BrO radicals. This mechanism should be particularly efficient in the presence of the high concentrations of sulphuric acid aerosols observed during ozone depletion events[3].

The chemical cycling of inorganic bromine (Br_x) in the troposphere is summarized in Fig. 1. The reaction of Br atoms with ozone, followed by the self-reaction of the BrO produced, represents a catalytic loss mechanism for ozone as Br is regenerated. Concentrations of Br_x collected on filters during ozone depletion events in the Arctic[1-3] are typically 25–100 parts per 10^{12} volume (p.p.t.v.). The composition of this 'filterable' bromine is uncertain; it probably includes HBr, $BrNO_3$, and Br, it may include BrO and HOBr, but it excludes most of Br_2 (ref. 5). If all of the filterable bromine were present in the form of Br and BrO, then ozone depletion over a few days could be readily accounted for by the rate of the BrO + BrO reaction[8]. But gas-phase chemistry models for Arctic surface air indicate that Br_x should be present mostly as the nonradical species HBr, HOBr and $BrNO_3$, resulting in little ozone loss[1]:

In a photochemical model study, McConnell *et al.*[7] suggested that the Br_x species could be scavenged by aerosols and photochemically converted to Br_2 in the aerosol phase, with sub-sequent volatilization of Br_2 and photolysis of Br_2 to Br. The mechanism for this aerosol-phase production of Br_2 was not described.

The rapid production of Br_2 from reaction of HOBr with Br^- in acid solution has been documented[9] under laboratory conditions.

$$HOBr_{(aq)} + Br^- + H^+ \rightarrow Br_{2(aq)} + H_2O \qquad (1)$$
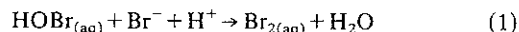
Forward and reverse reaction rate constants measured at 293 K and 0.1 M ionic strength are $k_f = 1.6 \times 10^{10}\,M^{-2}\,s^{-1}$ and $k_b = 110\,s^{-1}$. We expect the forward reaction (1) to be rapid during ozone depletion events owing to the high concentration of bromine, the abundance of acidic aerosol, and the high solubilities of HBr and HOBr. Surface air over the Arctic in the spring is ubiquitously affected by high concentrations of aqueous sulphuric acid aerosol transported from Eurasia[10]. Sulphate concentrations are typically 3 $\mu g\,m^{-3}$, and the sulphate aerosol acidity is equivalent to about half of that amount[10,11]; the aerosol pH is about 0 (ref. 12). Measurements taken during ozone depletion events indicate persistently high levels of sulphuric acid aerosol[3,10]. Even at pH 0, HBr is highly soluble; the Henry's law constant for $HBr_{(g)} \rightleftharpoons Br^- + H^+$ at 240 K is $5.8 \times 10^{12}\,M^2\,atm^{-1}$ (ref. 13). We are not aware of solubility data for HOBr, but expect the solubility to be larger than that of HOCl (the Henry's law constant for $HOCl_{(g)} \rightleftharpoons HOCl_{(aq)}$ at 240 K is $\sim 2 \times 10^3\,M\,atm^{-1}$; ref. 14). The characteristic time for the
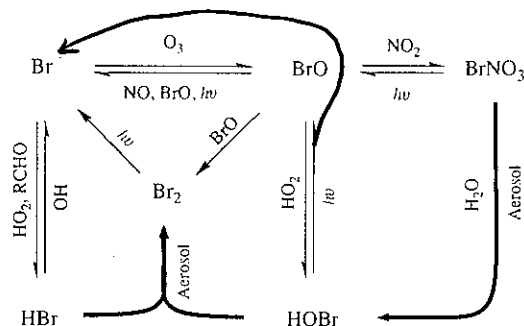

FIG. 1 Chemical cycling of inorganic bromine in the troposphere. Thin lines indicate gas-phase reactions; data for these reactions can be found in ref. 8. The aerosol reactions (1) and (2) discussed in the text are shown as heavy lines. The sequence of reactions $Br + O_3 \rightarrow BrO + O_2$ followed by $BrO + BrO \rightarrow 2Br + O_2$ represents a catalytic loss mechanism for ozone.
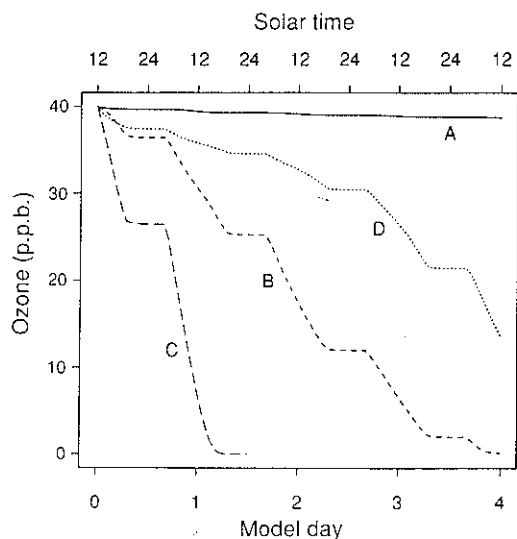
Solar time

FIG. 2 Ozone losses computed in the photochemical model for a surface-air parcel in Arctic spring (82.5° N, 1 April). The initial ozone concentration in the air parcel is 40 p.p.b.v. Simulation A includes gas-phase chemistry only, with initial conditions 50 p.p.t.v. inorganic bromine (Br_x) and 50 p.p.t.v. NO_x. Simulations B–D include aerosol reactions (1) and (2), with initial conditions: B, 50 p.p.t.v. Br_x and 50 p.p.t.v. NO_x; C, 100 p.p.t.v. Br_x and 50 p.p.t.v. NO_x; D, 50 p.p.t.v. Br_x and 1 p.p.t.v. NO_x.

forward reaction (1), calculated from the above data and assuming phase equilibrium for the nonlimiting reactant (either HOBr or HBr), is several orders of magnitude shorter than the characteristic time for gas-phase diffusion of the limiting reactant to the aerosol surfaces ($\sim 10^3$ s; ref. 15). We conclude that the production of $Br_{2(aq)}$ by reaction (1) is limited by the rate of uptake of either HBr or HOBr by the aerosol. Ionic strength corrections could not be large enough to modify our conclusion. Data for the analogous reaction involving Cl species in concentrated sulphuric acid indicate that there is little effect of ionic strength on reaction rate[9,14].

As $Br_{2(aq)}$ is produced it volatilizes to the gas phase; the Henry's law constant is low, 20 M atm^{-1} at 240 K (ref. 16). It can be inferred that hydrolysis of $Br_{2(aq)}$ by the reverse reaction (1) is too slow to compete with volatilization; the characteristic time for molecular diffusion out of typical 1-μm-diameter aerosol particles is $\sim 10^{-4}$ s (ref. 15). The gas-phase Br_2 is rapidly photolysed during daytime (time constant ~ 1 min), but it may accumulate at night.

Reaction (1) also provides a means for recycling $BrNO_3$ produced in the gas phase by the reaction $BrO + NO_2$ (Fig. 1). We expect that $BrNO_3$ should be rapidly scavenged by the aerosol and hydrolysed to HOBr, by analogy with data for $ClNO_3$ (ref. 14)

$$BrNO_{3(g)} \xrightarrow{H_2O} HOBr_{(aq)} + HNO_{3(aq)} \qquad (2)$$
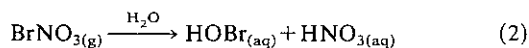
followed by subsequent reaction of $HOBr_{(aq)}$ and Br^- by (1) to produce Br_2.

We examined the contributions of reactions (1) and (2) to ozone depletion in the Arctic using a photochemical box model[17] applied to a surface-air parcel at Alert, Canada (82.5° N). The model was initialized at the onset of an ozone depletion event with the following air composition taken from typical measurements at Alert[3]: 40 parts per 10^9 (p.p.b.v.) ozone, 50 p.p.t.v. NO_x ($NO + NO_2$), 100 p.p.b.v. CO, 40 p.p.t.v. formaldehyde, 60 p.p.t.v. acetaldehyde, and 50 p.p.t.v. Br_x assumed to be present initially as BrO. The chemical evolution of the air parcel was computed for several model days, starting at noon, using kinetic and photochemical data from recent compilations[8,18-20].

The rate of reaction (1) was computed as the gas-phase diffusion flux[21] of the limiting species (HOBr, $BrNO_3$ or HBr) to a sulphate aerosol with a size distribution taken from mean observations for April, at the site[10]. The rate of reaction (2) was computed as the gas-phase diffusion flux of $BrNO_3$ to the aerosol. The diffusion flux depends in part on the sticking probability, α, of the gas at the aerosol surface. We estimate $\alpha = 0.01$ for HOBr and $BrNO_3$, and $\alpha = 0.3$ for HBr, on the basis of data for the corresponding Cl species over water/H_2SO_4 solutions[14,22]; these estimates are probably conservative. The resulting time-constants for gas uptake by the aerosol are 7×10^3 s for HOBr, 8×10^3 s for $BrNO_3$, and 5×10^2 s for HBr. Photon intensities were calculated for clear-sky conditions on 1 April; the 8-h twilight on 1 April was treated in the model as darkness. A fixed temperature of 240 K and a relative humidity of 75% were assumed.

The computed ozone losses are shown in Fig. 2. When only gas-phase chemistry is considered (simulation A), HBr sequesters the bromine, and ozone depletion is only a few per cent after four model days. In contrast, near-total ozone depletion is rapidly achieved when reactions (1) and (2) are considered; the depletion requires a few days with 50 p.p.t.v. Br_x (simulation B) and less than a day with 100 p.p.t.v. Br_x (simulation C). We find in simulations B and C that BrO dominates the bromine pool in the daytime (Fig. 3) because of rapid regeneration of Br and BrO radicals through reaction (1). At night BrO is depleted by a minor branch of the self-reaction producing Br_2 (Fig. 1), and Br_2 becomes the dominant bromine species. Filterable bromine was found to be formed when nighttime air from Barrow (Alaska) was exposed to artificial solar radiation[5]; this would be consistent with our mechanism if BrO were collected as filterable bromine. We predict here that little Br_x should remain on the aerosol throughout rapid ozone depletion events; a light-sensitive source of Br_2 (ref. 7) would cause Br_x to be present mostly on the aerosol at night.

The regeneration of bromine radicals by reaction (1) is contingent on a sustained supply of HBr and HOBr. We found in simulations B and C that the rate of reaction (1) is limited during the first two days by the supply of HOBr and that HBr becomes limiting later as the aldehydes are depleted. Near-total loss of NO_x takes place during the first day of simulation, reflecting the rapid formation of $BrNO_3$ followed by reaction (2) producing HNO_3. This result is consistent with observations indicating low concentrations of NO_x during ozone depletion events[3].
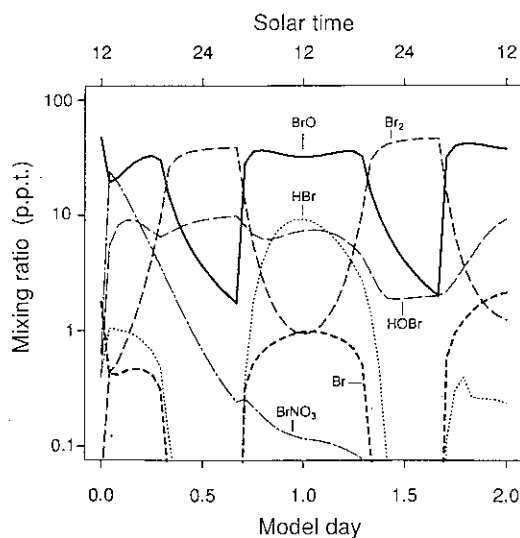

FIG. 3 Partitioning of inorganic bromine species in simulation B, for the first two days of simulation.

Sensitivity calculations for the air parcel with 50 p.p.t.v. Br_x (simulation B) show that ozone depletion can take place over a wide range of model conditions. A calculation with low initial NO_x (1 p.p.t.v.) indicates slow ozone loss during the first two days, because HOBr is not supplied by $BrNO_3$ hydrolysis, but the loss rate increases after the second day as depletion of the aldehydes moderates the source of HBr (simulation D; Fig. 3). Absence of aldehydes in the initial atmosphere has only a small effect on computed ozone loss because the reaction $Br + HO_2$ sustains a source of HBr that allows reaction (1) to proceed. Decreasing the sticking coefficients of HOBr and $BrNO_3$ from 0.01 to 0.001 slows down ozone loss, but near-total ozone deple-tion is still achieved within a week. Changing the HOBr photoly-sis rate constant by a factor of two, to reflect current uncer-tainty[4,19], does not affect results significantly.

Improved field data for the speciation of bromine during ozone depletion episodes are evidently needed to evaluate our hypothesis. Measurements of the BrO concentration would in particular allow a direct assessment of the rate of bromine-catalysed ozone loss. Measurements of the Br_2 concentration at night would allow us to distinguish between a light-sensitive source of Br_2 (resulting in night-time Br_x being present mostly as aerosol[7]) and a light-insensitive source, as proposed here. □

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