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Distribution of halon-1211 in the upper troposphere and lower stratosphere and the 1994 total bromine budget

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Abstract

We report here on the details of the first, in situ, real-time measurements of H-1211 ($CBrClF_2$) and sulfur hexafluoride (SF_6) mixing ratios in the stratosphere up to 20 km. Stratospheric air was analyzed for these gases and others with a new gas chromatograph (GC), flown aboard a National Aeronautics and Space Administration (NASA) ER-2 aircraft as part of the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) mission conducted in 1994. The mixing ratio of SF_6, with its approximately, linearly increasing tropospheric mixing ratio, was used to estimate the mean age of stratospheric air parcels along the ER-2 flight path. Measurements of H-1211 and mean age were then combined with simultaneous measurements of CFC-11 (CCl_3F), measurements of brominated compounds in stratospheric whole air samples, and records of tropospheric organic bromine mixing ratios to calculate the dry mixing ratio of total bromine in the lower stratosphere and its partitioning between organic and inorganic forms. The calculated amount of total bromine contained in midlatitude, stratospheric air parcels varied with the mean age of the sampled air. The oldest air parcel that was sampled had a mean age of six years and contained an estimated 16.4 ±2 pmol/mol (ppt) of bromine, whereas air parcels that had recently entered the stratosphere contained 18.2 ±2 ppt of bromine. We estimate that the organic, bromine-containing species were almost completely photolyzed to inorganic species in the oldest air parcels sampled. Our results for inorganic bromine are consistent with those obtained from a photochemical, steady-state model for stratospheric air parcels with CFC-11 mixing ratios greater than 150 ppt. For stratospheric air parcels with CFC-11 mixing ratios less than 50 ppt (mean age ≥ 5 years) we calculate inorganic bromine mixing ratios that are approximately 20% less than the photochemical, steady-state model. There is a 20% reduction in calculated ozone loss resulting from bromine chemistry in old air relative to previous estimates as a result of the lower bromine levels.

Introduction

Concern over the contribution of bromine to stratospheric ozone loss in polar regions [*McElroy et al.*, 1986; *Salawitch et al.*, 1988; *Anderson et al.*, 1989] and in midlatitudes [*Yung et al.*, 1980; *Garcia and Solomon,* 1994; *Wennberg et al.*, 1994] has resulted in international regulation of the production of halons and methyl bromide (CH_3Br) [*United Nations Environmental Program,* 1995]. The concentration of bromine in the stratosphere is about two orders of magnitude smaller than the concentration of chlorine, but bromine is 40-100 times more efficient at destroying ozone than is chlorine [*Garcia and Solomon*, 1994; *Solomon et al.*, 1995]. Bromine accounts for 20-40% of the annual loss of stratospheric ozone in polar regions [*Anderson et al.*, 1989; *Salawitch et al.*, 1993] and plays a significant role in midlatitude ozone loss at altitudes below 20 km [*Garcia and Solomon*, 1994; *Lary*, 1996a].

Organic compounds containing bromine are released at Earth's surface (Table 1), mix rapidly in the troposphere, and are advected into the stratosphere where photolysis and reaction with OH lead to the formation of inorganic bromine species. It is the inorganic species that participate in the catalytic destruction of ozone. A recent modeling study found that at an altitude of 20 km in the midlatitudes, the inorganic bromine species, Br_2, BrO, BrONO, BrCl, $BrONO_2$, and HOBr, have lifetimes in sunlight of less than one hour [*Lary*, 1996a]. The model results indicate that the longest-lived inorganic bromine species is HBr with a lifetime of one day. The model results also suggest that only one percent of the inorganic bromine is in the form of HBr and that approximately one half of inorganic bromine is present as BrO in sunlight in the lower stratosphere [*Lary*, 1996a]. Although inorganic bromine is involved in catalytic ozone destruction in the absence of reactive nitrogen, hydrogen, and chlorine species, bromine also participates in “mixed-family” cycles of catalytic ozone destruction. In addition to producing ozone loss, the “mixed-family” reactions influence the partitioning within the bromine, chlorine, nitrogen, and hydrogen families [*Danilin and McConnell,* 1995; *Lary et al.*, 1996b] which makes the contribution of bromine to ozone loss depend strongly upon local conditions [*Garcia and Solomon*, 1994; *Danilin et al.*, 1996]. It is important to note that our understanding of bromine chemistry in the stratosphere is not yet complete as evidenced by the significant changes and additions for bromine chemistry between the JPL-94 and JPL-97 recommendations [*DeMore et al.*, 1994; 1997].

Halons, which are purely anthropogenic compounds used primarily as fire suppressants, and CH_3Br, a naturally occurring compound that is also manufactured and used as a fumigant, are the major sources of stratospheric bromine (Table 2). The halons contribute about one third of the total bromine entering the stratosphere. The sale and manufacture of halons was banned in developed countries on January 1, 1994 and is scheduled to be banned in developing countries by 2010 [*United Nations Environmental Program,* 1995]. Halons have been stockpiled and their use limited to critical applications such as archive protection and passenger protection aboard airplanes, ships, and military vehicles. Although the tropospheric mixing ratios of the two most abundant halons, H-1211 and H-1301 ($CBrF_3$), continue to rise, their tropospheric growth rates have recenly slowed [*Butler et al.*, 1992; *Montzka et al.*, 1996; *Butler et al.*, 1997]. The largest single source of stratospheric bromine, CH_3Br, has a tropospheric mixing ratio of 9.8 ±0.6 ppt [*Lobert et al.*, 1995; *Penkett et al*., 1995]. Methyl bromide is produced and destroyed by a variety of physical and biological processes on land and in the ocean. The release of CH_3Br to the atmosphere during fumigation is the largest anthropogenic source of CH_3Br; smaller contributions arise from biomass burning and use of leaded fuel additives. Naturally occurring CH_3Br is believed to account for 60-80% of the total atmospheric burden of methyl bromide [*Butler and Rodriguez*, 1996; *Penkett et al.*, 1995]. Additional source gases include the relatively short-lived species, dibromomethane (CH_2Br_2) and bromochloromethane (CH_2BrCl), which have atmospheric lifetimes on the order of a year and tropospheric mixing ratios of 1.1 and 0.14 ppt (Tables 1 and 2). Several other naturally occurring, organic, brominated compounds have been measured in the troposphere, but they are short-lived in the atmosphere and are believed to be insignificant contributors to stratospheric bromine (Table 1).

The amount of bromine in the stratosphere and its partitioning among inorganic and organic species are crucial inputs for atmospheric models that attempt to simulate the distribution of ozone and evaluate the impact of HO_x, NO_x, and halogen chemistry on ozone destruction [*Salawitch et al.*, 1993; *Wennberg et al.*, 1994, 1997; *Gao et al.*, 1996]. Currently, in situ techniques measure a limited number of brominated compounds from which total bromine is estimated. We calculate the total bromine in stratospheric air parcels by first determining the time series of bromine input to the stratosphere. The amount of bromine in an isolated, stratospheric air parcel remains constant at the value it had upon entry to the stratosphere, though photolysis and reaction with OH convert the organic source compounds to inorganic species as the parcel passes through the stratosphere. For a real air parcel, subject to large- and small-scale mixing processes in the atmosphere, the amount of bromine will reflect contributions from air parcels that entered the stratosphere at different times. However, there remains a correlation between the total bromine and the mean age of the air parcel. The mean age of stratospheric air is determined from the measured mixing ratio of an age tracer such as SF_6. The amount of bromine present in organic forms is either measured directly or estimated from tracer-tracer correlations. The amount of inorganic bromine in an air parcel is then determined by subtracting the organic bromine from the total bromine. This method is based on measured mixing ratios of organic, brominated source compounds in both the troposphere and stratosphere and will therefore be referred to as the organic bromine method. An independent method for determining the amount of inorganic bromine in a stratospheric air parcel makes use of the rapid photochemical cycling among various inorganic, bromine-containing species in the sunlit stratosphere. This method is based on measurements of the solar radiation and mixing ratios of BrO and other radicals and will be referred to as the inorganic bromine method. Both methods were used to calculate the partitioning of bromine in the lower stratosphere from measurements taken during the ASHOE/MAESA mission.

Instrumentation

Mixing ratios of CFC-11, H-1211, SF_6 and seven other molecules were measured during the ASHOE/MAESA mission with the fully automated, four-channel GC, Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV) [*Elkins et al.*, 1996a]. Measurements of H-1211 and CFC-11 were obtained once every three minutes while SF_6 was measured every six minutes (Table 3). Calibrated air was sampled every fifteen minutes (every thirty minutes for SF_6) during flight to account for drift in instrument response. The in-flight calibration gases were secondary standards calibrated against the primary gravimetric standards prepared at the National Oceanic and Atmospheric Administration's Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) [*Elkins et al.,* 1993; 1996b]. Most of the measurements were obtained in the stratosphere at ER-2 cruise altitudes of 15-20 km, but a few tropospheric measurements were obtained upon ascent and descent of the aircraft (Figure 1). Measurements were taken in October and November 1994 at latitudes ranging from 70˚S to 60˚N.

All prior measurements of organic, bromine containing compounds in the stratosphere had been made by collecting whole air samples from aircraft or balloon platforms and storing them for analysis with ground-based instruments. In this work we incorporated measurements of brominated compounds in samples collected by researchers at the Jülich Research Center's Institute for Atmospheric Chemistry (KFA), the University of California at Irvine (UC-Irvine), and the National Center for Atmospheric Research (NCAR). Researchers at KFA designed a balloon-borne, neon-cooled cryo-sampler to collect 15 samples per flight. Bromine compounds were separated by gas chromatography and detected with a mass-selective detector (GC-MS) at the University of East Anglia (UEA). The KFA/UEA air samples were collected on four balloon flights in the Arctic and northern mid-latitudes, to heights of 32 km. Further details are given in *Schmidt et al.* [1987] and *Lee et al.* [1995]. Aircraft-based, whole air samplers were developed separately at UC-Irvine [*Blake et al.*, 1992] and NCAR [*Heidt et al.*, 1989]. The UC-Irvine sampler used 2 liter, stainless steel cans that were conditioned by baking them in air. After evacuation to 0.01 torr, two torr of purified water vapor was added to each canister prior to shipping the canisters to the field. Air samples were collected by filling the cans to approximately 40 psig with a two-stage, metal bellows pump. Gases were separated by gas chromatography and detected with an electron capture detector (GC-ECD) at UC-Irvine. The NCAR sampler used a four-stage, metal bellows pump to fill evacuated, 1.6 liter stainless steel cans. The NCAR cans were filled to approximately 40 psia. The technique of GC-MS was used to analyze the samples at NCAR. During the second Airborne Arctic Stratospheric Expedition (AASE II) the UC-Irvine sampler was deployed aboard a DC-8 and the NCAR sampler operated aboard an ER-2 [*Schauffler et al.*, 1993]. During the May 1995, Stratospheric Tracers for Atmospheric Transport (STRAT) mission, the NCAR sampler was again deployed aboard an ER-2 and samples were analyzed for six organic, bromine containing species.

There are several additional publications that report stratospheric profiles of bromine-containing compounds [*Fabian, et al.*, 1981; *Lal et al.*, 1985; *Singh et al.*, 1988; *Lal et al.*, 1994; *Fabian et al.*, 1994; *Kourtidis et al.*, 1996]. Data in these publications are from analysis of samples collected by a balloon-borne, neon-cooled, cryo-pumped sampler developed at the Max-Planck Institute for Aeronomy (MPAE). Our analysis method relies on correlations obtained from simultaneous measurements of brominated compounds and CFC-11. With the exception of *Fabian et al.* [1981], simultaneous measurements of CFC-11 were not reported so we have not included data from the MPAE samples in our analysis.

Stratospheric mixing ratios of a principal inorganic species, BrO, have been measured with ground and aircraft-based instruments. Resonance fluorescence detection of Br produced by the titration of BrO with NO was used to obtain in situ measurements of BrO during AASE [*Toohey et al.*, 1990], AASE II [*Avallone et al.*, 1995], and ASHOE/MAESA. Slant column abundances of BrO have been measured with instruments aboard aircraft [*Wahner et al.*, 1990] and balloons [*Pundt et al.*, 1996] and with ground-based instruments [*Carroll et al.*, 1989; *Solomon et al.*, 1989; *Arpag et al.*, 1994].

Procedure

Our procedure for determining the partitioning of stratospheric bromine between organic and inorganic components is conceptually the same as the procedure used to estimate inorganic chlorine in the stratosphere by *Woodbridge et al.* [1995]. The partitioning of bromine within an air parcel is given by equation (1).

$$[Br_{Total}] = [CBr_y] + [Br_y] \qquad (1)$$

By convention, Br_y designates bromine residing in inorganic species, CBr_y designates the bromine contained in organic bromine species, and the total amount of bromine is given by Br_{Total}. The use of square brackets indicates a mixing ratio rather than a concentration throughout this paper. The only significant source of bromine in the stratosphere is assumed to be organic bromine emitted at Earth's surface (Tables 1 and 2). We also assume that only those species with lifetimes in the troposphere that are long enough to allow them to be advected into the stratosphere (lifetime > 0.4 y) contribute to stratospheric bromine. In our calculation we assume that the stratospheric input function, Br_{Total}, is the sum of the bromine contained in the six species, CH_3Br, H-1211, H-1301, H-2402, CH_2Br_2, and CH_2BrCl (Table 2). First, the time series of the mixing ratios of these six compounds at Earth's surface was compiled. The use of surface measurements rather than measurements at the tropical tropopause sets an upper limit on how much bromine can be carried into the stratosphere by these species. Second, the mean age of air along the ER-2 flight path was estimated from measurements of SF_6, a long-lived, anthropogenic gas with a growth rate of approximately 6.7%/year [*Maiss et al.*, 1996; *Geller et al.*, 1997]. Combining the time series of surface measurements and mean age of air, the value of $[Br_{Total}]$ was estimated for each sampled air parcel. Third, mixing ratios of H-1211 and CFC-11 were measured along the ER-2 flight track. The mixing ratios of the five other source compounds were estimated from the measured mixing ratio of CFC-11 and their correlations with [CFC-11]. The value of $[CBr_y]$ was estimated for each sampled air parcel by summing the bromine contributed by each of the six source compounds. Finally, equation (1) was used to calculate $[Br_y]$.

Tropospheric Record of Source Gases

Halon measurements were obtained from weekly flask samples collected at the NOAA/CMDL background monitoring sites. Gases were separated by gas chromatography and detected either with an electron capture detector (GC-ECD) or a mass selective detector (GC-MS) [*Butler et al.*, 1992; *Montzka et al.*, 1996; *Butler et al.*, 1997]. Halon-1211 and H-1301 measurements began in mid-1989 and H-2402 measurements were initiated in 1995. Third order polynomials were fit to the data to obtain functions describing the tropospheric mixing ratios of H-1211 and H-1301 as a function of time. The time series of H-2402 flask measurements was augmented by GC-MS analysis of six archived air samples (collected from late 1991 to early 1994) and fit using a line [*Elkins et al.*, 1996b; *Butler et al.,* 1997] (Table 2).

We assumed that the global tropospheric mixing ratio of CH_3Br was 9.8 ±0.6 ppt and was constant over the six year period of interest with an estimated uncertainty in the growth rate of ±0.2 ppt/year [*Butler and Rodriguez*, 1996]. Our global estimate is based on measurements of CH_3Br in air that was sampled during a transect of the Pacific Ocean in early 1994 [*Lobert et al*., 1995]. *Lobert et al.* [1995] calculated average northern and southern hemisphere mixing ratios of 11.1 ppt and 8.5 ppt in agreement with other recent marine boundary layer measurements [*Penkett et al.,* 1995].

There are few published tropospheric measurements of CH_2Br_2 and CH_2BrCl. We assigned 1994 tropospheric mixing ratios of 1.1 ±0.2 ppt for CH_2Br_2 and 0.14 ±0.03 ppt for CH_2BrCl, based on NCAR analysis of air samples collected during the May 1995 STRAT campaign. There are no trend data available for the tropospheric mixing ratios of these two naturally produced compounds so we assumed that their tropospheric mixing ratios were constant over the six year period of interest. To compensate for this assumption, we adopted one standard deviation (1 s.d.) uncertainties of ±0.1 ppt/year and ±0.01 ppt/year in the trends of CH_2Br_2 and CH_2BrCl. This assumption encompasses extremes as the two standard deviation uncertainty includes the possibility that the tropospheric mixing ratios of these two compounds grew linearly from zero to their late 1994 tropospheric values over a period of six years.

The stratospheric input function for organic bromine is estimated as the sum of the bromine contained in six, long-lived, organic bromine species (Table 2) where the mixing ratio for each species is measured at the tropical tropopause. The time series for each source compound given in Table 2 is based upon measurements taken at Earth's surface. We assume that these species are well mixed in the troposphere so that any vertical gradient in the mixing ratios of these species is the result of increasing concentrations at Earth's surface. If the mixing ratios of the source molecules are measured at Earth's surface then the stratospheric input function at time t, $[Br_{Total}](t)$, is the total amount of bromine contained in the source molecules at time $t - \delta\Gamma$ where $\delta\Gamma$ is the time required for the global surface average to reach the tropical tropopause. For t in years between 1988 and 1996 we calculate the stratospheric input function to be

$$[Br_{Total}](t) = [CH_3Br](t - \delta\Gamma) + [H\text{-}1211](t - \delta\Gamma) + [H\text{-}1301](t - \delta\Gamma) + 2[CH_2Br_2](t - \delta\Gamma) + 2[H\text{-}2402](t - \delta\Gamma) + [CH_2BrCl](t - \delta\Gamma) \qquad (2)$$

$$[Br_{Total}](t) = 18.48 + 0.286(t - \delta\Gamma - 1994.875) - 0.0091(t - \delta\Gamma - 1994.875)^2 \qquad (3)$$

where all mixing ratios are in ppt. The halons are assumed to account for 100% of the increase in tropospheric mixing ratios of compounds that contribute to stratospheric bromine (Table 2, Figure 2). The uncertainty in $[Br_{Total}]$ was calculated from the uncertainties in the late-1994, tropospheric measurements and the uncertainties in the tropospheric trends of each species.

Mean Age of Air

Species with no appreciable sources or sinks in the stratosphere that also have linearly increasing tropospheric mixing ratios can be used to determine the mean age of air in stratospheric air parcels [*Hall and Plumb*, 1994]. Use of a conservative tracer allows one to evaluate the mean age of an air parcel by comparing the measured mixing ratio in the stratospheric parcel to a time series of tropospheric mixing ratios. The mean age of air can be estimated from the mixing ratios of several different tracers, including CO_2, CFC-115, and SF_6 [*Woodbridge et al.,* 1995; *Daniel et al.*, 1996; *Harnisch et al.*, 1996]. The relationship between the mean age, Γ, the stratospheric mixing ratio, [X], and the mixing ratio at the tropopause, $[X]_o$, is given by equation (4).

$$[X](\mathbf{x},t) = [X]_o(t - \Gamma(\mathbf{x})) \quad (4)$$

The measurement in the stratosphere occurs at a point in space and time designated by ($\mathbf{x}$,t). The mean age is referenced from the tropopause. The mean age of air can not be obtained directly from measured mixing ratios of an age tracer if the time series of tropospheric mixing ratios for the age tracer is not linear. A complete discussion of the method for deriving the mean age of stratospheric air parcels from measurements of SF_6 can be found elsewhere [*Volk et al.*, 1997]. For a species with a quadratic trend equation (4) becomes

$$[X](\mathbf{x},t) = [X]_o(t - \Gamma(\mathbf{x})) + 2c\Delta^2(\mathbf{x},t) \quad (5)$$

where c is the quadratic coefficient describing the time series and Δ is the width of the age spectrum. The quantity, Δ^2, was estimated from global circulation models to be proportional to the mean age of air (equation (6), [*Volk et al.*, 1997]).

$$\Delta^2(\mathbf{x},t) = (1.25 \pm 0.5)(\Gamma(\mathbf{x},t) + \delta\Gamma) \quad (6)$$

The presence of a quadratic term in the time series produces a deviation away from the strictly linear case that is proportional to the quadratic coefficient and the mean age of the air. Sulfur hexafluoride is a purely anthropogenic compound that is used widely as an electrical insulator in transformers and high voltage switching devices. Very small amounts have also been released during tracer studies. It has no known tropospheric sinks and a stratospheric lifetime of approximately 3200 years [*Ravishankara et al.*, 1993]. The recent trend in global, surface mixing ratios of SF_6 is slightly nonlinear [*Geller et al.*, 1997].

$$[SF_6]_{surface}(t) = 3.4361 + 0.2376(t - 1996) + 0.0049(t - 1996)^2 \quad (7)$$

Equation (7) is valid for 1987 < t (years) < 1997. The mixing ratio of SF_6 at the tropical tropopause will be less than that at the surface due to the increasing surface mixing ratios, the finite mixing time between the hemispheres, and the finite transport time from Earth’s surface to the tropical tropopause. The mixing ratio of SF_6 at the tropical tropopause was 3 ppt in late 1994 and the global surface average was approximately 3.18 ppt. The 0.18 ppt difference represents a time shift of 0.8 y [*Volk et al.*, 1997; *Boering et al.*, 1996]. Thus we adopt the value of 0.8 years for the transit time, δΓ, of the global surface average to the tropopause. Only those bromine containing species with time-dependent tropospheric mixing ratios (halons) have contributions to total bromine that are affected by the choice of δΓ. Uncertainty in δΓ of ± 0.5 y results in a -/+ 0.14 ppt uncertainty in total bromine. The time series for SF_6

mixing ratios at the tropical tropopause is given by

$$[SF_6]_{tropopause}(t) = 3.4361 + 0.2376((t - 0.8) - 1996) + 0.0049((t - 0.8) - 1996)^2. \quad (8)$$

We chose mid-October 1994 as our reference time because this time coincides with the in situ, stratospheric measurements taken during the ASHOE/MAESA mission. Combining equations (5), (6), and (8) and using 1994.875 y and 0.8 y for t and $\delta\Gamma$ yields the following relationship between $[SF_6]_{strat}$ and mean age of air for stratospheric air parcels sampled during the fourth deployment of ASHOE/MAESA (altitudes < 21 km).

$$[SF_6]_{strat} = 3.4459 + 0.2376(t - \Gamma - 0.8 - 1996) + 0.0049(t - \Gamma - 0.8 - 1996)^2 + (0.01225\Gamma) \quad (9)$$

The mean age of air, Γ, in terms of the SF_6 mixing ratio in a stratospheric air parcel, $[SF_6]_{strat}$, is given by equation (10). Equation (10) is a fit to the data taken near the end of 1994 and is valid only for that time period. To solve for the relationship between measured $[SF_6]_{strat}$ and Γ at a future measurement time, t, equation (9) can be inverted analytically to yield Γ as a function of $[SF_6]_{strat}$.

$$\Gamma = 22.514 - 10.345[SF_6]_{strat} + 0.9533[SF_6]^2_{strat} \quad (10)$$

Equations (9) and (10) are representative of the lower 1994 stratosphere and are based upon SF_6 mixing ratios measured along the ER-2 flight track. The uncertainty in the derived mean age owing to the precision of the stratospheric $[SF_6]$ measurements is ±4 months (1 s.d.). The mean age of the oldest air parcel sampled during ASHOE/MAESA was about 6 years, which corresponds to entry into the stratosphere near the end of 1988.

The chromatography used to separate SF_6 resulted in a sampling frequency that was one half that of H-1211 and CFC-11. To complete our SF_6 data set we used [CFC-11] as a proxy for $[SF_6]$, based upon the correlation of $[SF_6]$ and [CFC-11] during flights in which H-1211 was also measured (equation (11)).

$$[SF_6] = 2.0379 + 0.001235[CFC\text{-}11] + 8 \times 10^{-6}[CFC\text{-}11]^2 \quad (11)$$

Equation (11) is a second order polynomial fit to all data, including data taken in the tropics, with each data point weighed equally. This correlation, which forms a snapshot of the relationship between SF_6 and CFC-11 at the end of 1994, will change with changes in the tropospheric mixing ratios of these two compounds.

Estimates for Brominated Source Species Not Measured During ASHOE/MAESA

Correlations of brominated species with CFC-11 were compiled from analyses of whole air samples collected by the UC-Irvine (DC-8, 1992), UEA/KFA (four balloon flights from March 1993 to July 1994), and NCAR (ER-2, 1995) samplers. As previously mentioned, the correlation between two species will depend in part upon the tropospheric mixing ratio of each species. The three groups did not measure the same tropospheric mixing ratios of the various brominated compounds (Table 4), and the spread in the measurements exceeds the observed global trend for each species over the measurement time period. Thus we would not expect correlations obtained by different groups to be in good agreement. The spread in measurements may arise from real atmospheric variability, a systematic error in the measurements, or simply a scalar calibration error. Each laboratory used an independent calibration scale which could account for the spread in the measurements. Scalar calibration differences can be resolved by applying a species and lab dependent normalization factor to the original measurements. We normalized the data from different research groups so that each species had a normalized value of one at the tropopause. The normalized correlations obtained by the various groups were in much better agreement than the unnormalized correlations. The scatter in the normalized correlations is the result of measurement uncertainty and atmospheric variability (Figure 3). There are not enough data to extract the seasonal and spatial dependencies of the atmospheric variability which prevents precise parameterization of the correlations. For this reason we combined all data and chose to describe each correlation using a single parameter.

A simple parameterization of the relationship between the mixing ratio of a species at the tropopause, $[X]_o$, and the mixing ratio of the species in the stratosphere, [X], is given by equation (12).

$$[X] = [X]_o \exp(-t/\tau_X) \qquad (12)$$

The quantity, $1/\tau_X$, is an effective stratospheric loss rate. For the species being considered, the dominant loss mechanism is photolysis. The correlation between two species with stratospheric mixing ratios that are well represented by equation (12) is a power law relationship with a power coefficient equal to the ratio of the lifetimes of the two species. The correlations between the brominated species and CFC-11 are adequately described by a simple power law (equation (13), Figure 3).

$$[X]/[X]_o = ([\text{CFC-11}]/[\text{CFC-11}]_o)^{1/d} \qquad (13)$$

The mixing ratio of each brominated species is represented by [X], the subscript, o, designates the mid-October 1994 mixing ratio at the tropopause, and (1/d) is the power coefficient (Table 4, Figure 3). While not rigorously accurate, the value of d provides an estimate of the lifetime of each species relative to that of CFC-11. These correlations were obtained by weighing each data point equally, including data taken in the tropics. For air parcels sampled along the flight track of the ER-2, $[CBr_y]$ was calculated from the direct measurement of H-1211 and estimates of the mixing ratios of the five unmeasured organic bromine species from correlations with CFC-11. The uncertainty in [CBr_y] was calculated from the uncertainty in the measurements of the late-1994, tropospheric mixing ratios (Table 2) and the uncertainty in the value of d for each species (Table 4). The uncertainties are one standard deviation values. The uncertainty in the CFC-11 measurement was negligible and was not included in our estimate of the total organic bromine in an air parcel.

In the absence of measurements of brominated compounds, the correlations can be calculated from two-dimensional models that accurately represent radiative, chemical, and dynamic processes in the atmosphere. The Atmospheric Environmental Research, Inc. (AER) model, which incorporates restricted exchange between the tropics and midlatitudes in the lower stratosphere [*Weisenstein et al.*, 1996], was used to calculate correlations of the halons and CH_3Br with CFC-11. The tropospheric mixing ratios of the three halons and CH_3Br used in our calculation of total bromine (Table 2) were used to generate a time-dependent, bromine source function for the AER model. For the purposes of comparison, equation (13) was used to fit the model results that matched the season and location of the NCAR data. Agreement between the modeled and observed correlations is good (Figure 3). This suggests that the degradation of the source molecules is well represented by the model.

Organic bromine can also be estimated solely from measurements of [CFC-11] if the correlation between [H-1211] and [CFC-11] is used rather than measured H-1211 mixing ratios. Then, the relationship between [CBr_y] and [CFC-11] is given by

$$\begin{aligned}[CBr_y] = {} & [CH_3Br]_o\ [\text{CFC-11}]/[\text{CFC-11}]_o^{(1/0.67)} + [\text{H-1211}]_o\ [\text{CFC-11}]/[\text{CFC-11}]_o^{(1/0.60)} \\ & + [\text{H-1301}]_o\ [\text{CFC-11}]/[\text{CFC-11}]_o^{(1/0.98)} + 2[\text{H-2402}]_o\ [\text{CFC-11}]/[\text{CFC-11}]_o^{(1/0.65)} \\ & + 2[CH_2Br_2]_o\ [\text{CFC-11}]/[\text{CFC-11}]_o^{(1/0.12)} + [CH_2BrCl]_o[\text{CFC-11}]/[\text{CFC-11}]_o^{(1/0.16)}. \qquad (14)\end{aligned}$$

where the subscript, o, designates a mixing ratio at the tropical tropopause. As before, the denominator of the power coefficient, d, multiplied by the lifetime of CFC-11 yields an estimate of the lifetime of each brominated compound. An "effective lifetime" of 26 years (d=0.58) is obtained for CBr_y when equation (14) is reparameterized in the form of the power law function given in equation (13) (Figure 4). The "effective lifetime" of CBr_y is based upon a CFC-11 lifetime of 45 years [*Volk et al.*, 1997].

The correlations discussed above were based upon the mixing ratio of CFC-11 rather than that of nitrous oxide (N_2O) because the lifetimes of the brominated source compounds are closer to the lifetime of CFC-11 than to the lifetime of N_2O. However, the same methods could have been applied to measurements of N_2O, which were obtained every six minutes by GC-MS and at 1 Hz using a tunable laser, absorption technique [*Podolske and Loewenstein*, 1993] during ASHOE/MAESA. The following equations describe the relationship between the mixing ratios of CFC-11 and N_2O based upon measurements from the entire ASHOE/MAESA mission. The CFC-11 and N_2O measurements are from

ACATS-IV. The correlation between CFC-11 and N_2O varies with latitude so we have provided both tropical (-20° < latitude < 20°) and extratropical correlations. The correlation in the tropics is given by

$$[\text{CFC-11}] = 39.92 - 0.33539[N_2O] + 0.0033736[N_2O]^2 \qquad (15)$$

and is valid for N_2O mixing ratios between 225 and 310 ppb. The correlation in the midlatitudes is given by

$$[\text{CFC-11}] = 252.92 - 4.5591[N_2O] + 0.025644[N_2O]^2 - 3.4639 \ \mathrm{H} \ 10^{-5}[N_2O]^3 \qquad (16)$$

and is valid for N_2O mixing ratios between 130 and 310 ppb. The mixing ratio of CFC-11 is in ppt and the mixing ratio of N_2O is in parts per billion (ppb) for equations (15) and (16).

Results and Discussion

The observed distribution of H-1211 mixing ratios measured during ASHOE/MAESA was consistent with that expected for a species with an increasing tropospheric source and a stratospheric sink subject to Brewer-Dobson circulation (Figure 5). Air parcels sampled on ascent and descent (data points below 15 km) from Moffett Field, CA (37°N, 122°W), Barber's Point, HI (21°N, 158°W), Nadi, Fiji (18°S, 175°E), and Christchurch, New Zealand (43°S,172° E) show values consistent with late-1994 surface mixing ratios. At a given altitude, mixing ratios of H-1211 in the tropics were larger than those at higher latitudes, consistent with the upward advection of tropospheric air that contained high mixing ratios of H-1211 into the tropical stratosphere. The lowest H-1211 mixing ratios were observed in air parcels located at high altitudes. On the flight of October 13, 1994 low H-1211 mixing ratios were observed at 16 km when the ER-2 executed a dive near 68°S. This is consistent with downward advection of air in polar regions.

A similar picture emerged from the SF_6 measurements (data not shown). The highest values of $[SF_6]$ were observed in the tropics with a trend towards lower values with increasing altitude and latitude. The mean age of air calculated from the measurements of SF_6 (equation (10)) ranged from 0 to 6 years (Figure 6). At high northern and southern latitudes, air parcels were sampled below 18 km with mean ages greater than 4 years, which suggests downwelling of stratospheric air in these regions. There was only one air sample with a calculated age in excess of 6 years. In general, the oldest air parcels sampled had mean ages of 5 to 5.5 years.

We calculated $[Br_{Total}]$, $[CBr_y]$, and $[Br_y]$ in air parcels sampled along the ER-2 flight path for eight flights from October 13, 1994 to November 11, 1994 (Figure 7). The calculated value of $[Br_{Total}]$ in the 1994 lower stratosphere ranged from 16.4 to 18.2 ppt with the oldest air parcels containing approximately 2 ppt less bromine than the youngest air parcels (Figure 7). The uncertainty in $[Br_{Total}]$ is approximately ±2 ppt over the entire range of Br_{Total} values. Approximately one half of the uncertainty is due to the uncertainty associated with the individual measurements of the six organic bromine species and the other half arises from the uncertainty in the time series of surface mixing ratios for each species. Equations (17)-(19) are fits to the calculated results for $[Br_{Total}]$, $[CBr_y]$, and $[Br_y]$ (Figure 7).

$$[Br_{Total}](t = 1994.875) = 16.35 + 0.0043[CFC\text{-}11] + 9.5 \times 10^{-6}[CFC\text{-}11]^2 \qquad (17)$$

$$[CBr_y](t = 1994.875) = 0.33 + 0.001[CFC\text{-}11] + 0.00054[CFC\text{-}11]^2$$
$$- 2.55 \times 10^{-6}[CFC\text{-}11]^3 + 5.37 \times 10^{-9}[CFC\text{-}11]^4 \qquad (18)$$

$$[Br_y](t = 1994.875) = 16.02 + 0.0033[CFC\text{-}11] - 5.305 \times 10^{-4}[CFC\text{-}11]^2$$
$$+ 2.55 \times 10^{-6}[CFC\text{-}11]^3 - 5.37 \times 10^{-9}[CFC\text{-}11]^4 \qquad (19)$$

Equations (20) and (21) can be used to calculate $[Br_{Total}]$ and $[CBr_y]$ for stratospheric measurements taken at time, t, after 1994.875. Equation (21) gives $[Br_{Total}]$ in an air parcel as a function of mean age of the air parcel.

$$[Br_{Total}] = 18.48 + 0.286(t - \Gamma - \delta\Gamma - 1994.875) - 0.009(t - \Gamma - \delta\Gamma - 1994.875)^2 \qquad (21)$$

$$[CBr_y] = 9.8([CFC\text{-}11]/[CFC\text{-}11]_o)^{(1/0.67)}$$
$$+ (2.25 + 0.115(t - 1994.875) - 0.0055(t - 1994.875)^2)([CFC\text{-}11]/[CFC\text{-}11]_o)^{(1/0.98)}$$
$$+ (2.25 + 0.115(t - 1994.875) - 0.0055(t - 1994.875)^2)([CFC\text{-}11]/[CFC\text{-}11]_o)^{(1/0.98)}$$
$$+ (0.47 + 0.010(t - 1994.875))([CFC\text{-}11]/[CFC\text{-}11]_o)^{(1/0.65)}$$
$$+ 1.1([CFC\text{-}11]/[CFC\text{-}11]_o)^{(1/0.12)} + 0.14([CFC\text{-}11]/[CFC\text{-}11]_o)^{(1/0.16)} \qquad (22)$$

The amount of bromine that resides in inorganic forms can be calculated from the difference of $[Br_{Total}]$ and $[CBr_y]$. Equation (23) can be used to calculate the mean age, $\Gamma(t)$, from a stratospheric measurement of $[SF_6]$ at time, t (in years).

$$\Gamma(t) = -1973.81 + t - 102.041\mathrm{sqrt}(0.462675 + 0.0196[SF_6] - 0.0002401t) \qquad (23)$$

Inclusion of bromine chemistry in photochemical models is important in calculating ozone loss rates. It is of interest here to compare total inorganic bromine from previous model studies to that calculated in this paper. One model that has gained wide acceptance for analysis of aircraft and satellite data is a photochemical, steady-state model used by Harvard University and the Jet Propulsion Laboratory (JPL) [e.g. *Salawitch et al.,* 1994; *Wennberg et al.,* 1997; *Gao et al.,* 1997; *Osterman et al.*, 1997]. The model calculates inorganic bromine using a method similar to the one we have described. The model incorporated NCAR WAS data from AASE II measurements of organic bromine species including CH_3Br, H-1211, H-1301, H-2402, and CH_2Br_2 [*Schauffler et al.*, 1993] to calculate total bromine. No age of the air mass correction was attempted because the uncertainty in the source gas measurements was too large to determine an atmospheric growth rate. The Harvard/JPL model used equation (24) to calculate total organic bromine from ACATS CFC-11 mixing ratios measured during AASE II.

$$[Br_y]_{Harvard/JPL} = 20.8682 - 4.3625 \times 10^{-2}[\text{CFC-11}] - 1.103 \times 10^{-4}[\text{CFC-11}]^2 \quad (24)$$

A comparison of our results with those produced by the Harvard/JPL model is shown in Figure 8. There is relatively good agreement for calculated mixing ratios of total inorganic bromine for CFC-11 mixing ratios greater than 150 ppt. However, there is a significant departure at CFC-11 < 150 ppt. One of the main reasons is that the Harvard/JPL fit used a total organic bromine at the tropopause of 21.1 ±0.8 ppt during AASE II [*Schauffler et al.*, 1993]. This value has been recently lowered to 17 ppt based on a recalibration of the measured concentrations of the organic source gases [*Daniel et al.*, 1996]. Another source of disagreement (~2 ppt) between our results and the Harvard/JPL fit can be explained by the model assumption that total bromine remained constant with time. The new formulation for Br_y presented here results in a ~20% reduction (for air parcels with [CFC-11] < 150 ppt) in the calculated abundance of BrO, and consequently ozone loss rates resulting from bromine chemistry, compared to the previous model studies that incorporated the Harvard/JPL fit for inorganic bromine.

Our estimate of Br_y can not be compared directly to the results obtained using measurements taken during AASE II [*Daniel et al.*, 1996] because of growth in the tropospheric mixing ratios of the halons that occurred between the two missions. The oldest stratospheric air parcels sampled during AASE II would have entered the stratosphere at the beginning of 1986, which predates the NOAA/CMDL record of source molecule mixing ratios at Earth's surface. If we linearly extrapolate the observed trend in surface mixing ratios between 1989 and 1991 back to 1986, we calculate a value of 15.3 ppt for $[Br_{Total}]$ in air parcels sampled during AASE II that were six years old in agreement with that obtained by *Daniel et al.* [1996]. Our calculated value of $[Br_{Total}]$ for 1992 is higher than that of *Daniel et al.* [1996] by 0.3 ppt, but well within the uncertainty of the measurements. Our calculation of bromine entering the stratosphere differs from that of *Daniel et al.* [1996] in that we used surface measurements for $[Br_{Total}]$ (shifted by the transit time from the surface to the tropopause) whereas *Daniel et al.* [1996] used measured mixing ratios at the tropical tropopause. Our method will overestimate the amount of bromine carried into the stratosphere if significant degradation of the source gases occurs in the troposphere. The uncertainty associated with our assumption that there is little degradation of the source gases in the troposphere is difficult to quantify. We expect species with short lifetimes to have more variable distributions than longer-lived species. The more variable the distribution, the harder it is to define a global average from a limited number of measurements. A few profiles of $[CH_2Br_2]$ and $[CH_2BrCl]$ in the troposphere have been measured by the authors (E.L.A and S.M.S) and they exhibit substantial variability. With the current measurements we estimate that tropospheric degradation of these two species does not exceed 50%. Profiles of [CH_3Br] in the troposphere (E.L.A. and S.M.S.) also exhibit some variability and from these profiles we estimate that the mixing ratio of CH_3Br at the tropopause differs from the global surface average by less than 10%. Our estimates of total bromine would be reduced by a little more than 2 ppt if significant degradation is occuring in the troposphere. The good agreement between our estimate of bromine at the tropical tropopause and the measured bromine at the tropical tropopause [*Daniel et al.* 1996] suggests that such degradation is not occuring.

Though organic, brominated compounds are the source of Br_y in the stratosphere, CBr_y is not directly involved in the catalytic cycles that destroy ozone. We estimated [CBr_y] from direct measurement of H-1211 and correlation of five other organic bromine species with CFC-11. The difference between [Br_{Total}] and [CBr_y] yields [Br_y]. In the oldest air parcels sampled, only 0.4 ppt (2.5%) of bromine remained in organic forms, indicating that the conversion of CBr_y to Br_y was essentially complete in those parcels. Air parcels that had recently entered the stratosphere contained 18.2 ppt of bromine, all of which was in the form of organic species. The values of [CBr_y] and [Br_y] were equal in air parcels with a mean age of 2.5 years. Our result for Br_y/Br_{Total} in the oldest sampled air parcels is slightly higher than that obtained by *Daniel et al.* [1996] (Table 5). Based upon the tropospheric mixing ratios and the lifetimes of the organic species that contribute to halogens in the stratosphere, we expect the conversion of organic bromine species to inorganic bromine species to be more complete than the analogous conversion of chlorine species in any given air parcel. Consistent with this, we calculate that the conversion of CBr_y to Br_y is more complete than the conversion of CCl_y to Cl_y in air parcels with similar ages (Table 5).

The results in Figure 7 and the accompanying equations and tables are representative of the lower stratosphere in late 1994. Since the results are expressed in terms of absolute mixing ratios, anticipated changes in tropospheric abundances of CFC-11, the halons, and CH_3Br will necessarily lead to modified relationships in the future. Although regulation of the halons will eventually reduce their tropospheric mixing ratios to zero, the minimum [Br_{Total}] in the stratosphere will ultimately be set by the tropospheric mixing ratios of naturally produced, brominated compounds. We estimate this burden to be approximately 9.2 ppt under the assumption that 70% of the CH_3Br burden [*Butler and Rodriguez*, 1996] and 100% of the CH_2Br_2 and CH_2BrCl burden in 1995 is the result of naturally occurring processes.

The suite of instruments aboard the ER-2 during ASHOE/MAESA provided a comprehensive set of data from which Br_y was calculated by an independent method which we refer to as the inorganic bromine method. This method was based on in situ measurements of the mixing ratios of HO_2, OH, ClO, NO, NO_2, and O_3 rather than long-lived tracers. In sunlight, rapid photolysis of $BrONO_2$, HOBr, BrO, and BrCl allows the use of a simple photochemical stationary state (PSS) model to calculate the partitioning of the inorganic bromine species BrO, $BrONO_2$, HOBr, HBr, Br, and BrCl. Photolysis rates are calculated from a radiative transfer model that takes into account variations in overhead ozone and albedo along the flight track. Rate constants and cross-sections are taken from the JPL 1997 evaluation. Inorganic bromine is estimated from in situ measurements of BrO in the stratosphere, $[BrO]_{in\ situ}$, and the calculated fraction, $([BrO]/[Br_y])_{PSS}$ (equation (24)).

$$[Br_y]_{inorganic\ method} = [BrO]_{in\ situ} / ([BrO]/[Br_y])_{PSS} \tag{24}$$

This method yields a value of $[Br_y]$ in the oldest air parcels sampled during ASHOE/MAESA of 20 (+11, -9.8) ppt, from a measured BrO mixing ratio of 11 (+4.5, -4.5) ppt. This value of [BrO] is higher than that observed during AASE and AASE II. However, data from a balloon-borne, uv-visible spectrometer launched from Andoya, Norway (70˚N,16˚E) in January 1996 yield BrO mixing ratios of 10 ppt at 20 km and 12 ppt at 21 km [*Pundt et al.*, 1996] in good agreement with [BrO] measured during ASHOE/MAESA. The inorganic bromine method relies on a thorough understanding of bromine chemistry in the stratosphere. Recent work by *Bogan et al.* [1996] suggests that the yield of HBr from the reaction of BrO and OH may be as much as 1%. Though this yield is small, a recent modeling study [*Chipperfield et al.*, 1997] suggests that a 1-2% yield of HBr would produce enough HBr to bring model results into better agreement with observations of HBr in the stratosphere [*Carlotti et al.*, 1995; *Johnson et al.*, 1995; *Nolt et al.*, 1997]. The observed HBr mixing ratio of 1 pptv near 20 km [*Nolt et al.*, 1997] is on the order of 5% of total Br_y rather than 1% and could influence the $[BrO]/[Br_y]$ ratio at a similar level. Simultaneous measurements of additional inorganic bromine species would be useful in addressing this issue as well as in evaluating our assumption that the inorganic bromine species are in photochemical equilibrium.

Although the values of $[Br_y]$ calculated with the inorganic bromine method agree with those calculated from the organic bromine method (Figure 8), the value of the intercomparison is lessened by the greater uncertainties inherent in the inorganic bromine method. The organic bromine method results in significantly less uncertainty. The values of $[Br_y]$ calculated with the inorganic bromine method are at the upper limit of what we would calculate from the organic bromine method. We note however, that there is a potential systematic error in our initial assumption regarding the source of stratospheric bromine (Table 2, equation (2)). If additional sources of stratospheric bromine are significant, our estimate of $[Br_{Total}]$, and thus $[Br_y]$, will be low.

The organic bromine method of calculating the total amount of bromine in the stratosphere works best for long-lived source gases which have negligible sinks in the troposphere. For these species, input to the stratosphere can be well parameterized by the global surface mean. Short-lived species which can exhibit large deviations away from a global average are not as well represented in our analysis. One such compound is bromoform ($CHBr_3$) which is naturally produced and has mixing ratios at Earth's surface between 0 and 10 ppt [*Penkett et al.*, 1985; *Cicerone et al.*, 1988; *Atlas et al.*, 1992]. Several measurements of $CHBr_3$ mixing ratios in excess of 20 pptv were obtained by *Class et al.* [1986] in a 1985 survey of halomethanes in marine air. Decomposition of 1 ppt of $CHBr_3$ in the stratosphere would increase $[Br_{Total}]$ by 3 ppt, which is more than 10% of the current input to the stratosphere. The lifetime of $CHBr_3$ is estimated to be on the order of weeks [*Penkett et al.*, 1985] so $CHBr_3$ was not included as a source of stratospheric bromine in our estimate of $[Br_{Total}]$. Bromoform mixing ratios of 0.1 ppt have recently been measured [*E. Atlas*, unpublished data, 1996] in whole air samples collected in the upper troposphere, but no bromoform has been measured in the stratosphere. Recent results from the AER, 2-D chemical transport model suggest that the organic species with lifetimes less than a month may be contributing appreciable amounts of bromine to the stratosphere (M. K. W. Ko et al., On the relation between stratospheric chlorine/bromine loading and short-lived tropospheric source gases, submitted to *J. Geophys. Res.*, 1997). Determining the amount of $CHBr_3$ and other short-lived, organic compounds of bromine, or inorganic bromine from their decomposition, entering the stratosphere remains an outstanding issue in the bromine budget of the lower atmosphere.

Conclusion

Stratospheric measurements of SF_6 were combined with the tropospheric time series of mixing ratios for six organic bromine species to calculate the amount of bromine in stratospheric air parcels sampled at latitudes between 70°S and 60°N to altitudes of 20 km during late-1994. The oldest air parcel sampled had a mean age of 6 years and contained an estimated 16.4 ±2 ppt of bromine. Air parcels that had recently entered the stratosphere contained an estimated 18.2 ±2 ppt of bromine. Total organic bromine in each air parcel was calculated from measurements of H-1211 and estimates of the remaining species based upon correlation with CFC-11 obtained from independent stratospheric data sets. The good agreement found between the observed correlations and those generated by a 2-D chemical transport model suggests that the conversion of organic to inorganic bromine in the stratosphere is reasonably well understood. Inorganic bromine was calculated from the difference between total bromine and organic bromine.

The method described in this paper yields estimates of $[Br_{Total}]$ and $[Br_y]$ in stratospheric air parcels with smaller uncertainty than other methods. The uncertainty could be reduced with more precise, global monitoring of brominated source gases at Earth's surface and an expanded measurement program for organic and inorganic bromine compounds in the lower atmosphere. Altitude profiles of short-lived organic bromine species, $CHBr_3$ in particular, from Earth's surface to the tropopause would be helpful in addressing this issue. Our method also presumes that strong, localized convection contributes negligible amounts of bromine to the stratosphere. Firmer conclusions are possible only after the contributions of short-lived organic bromine species to stratospheric bromine become better quantified.

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References

Anderson, J. G., W. H. Brune, S. A. Lloyd, D. W. Toohey, S. P. Sander, W. L. Starr, M. Loewenstein, and J. R. Podolske, Kinetics of O_3 destruction by ClO and BrO within the Antarctic vortex: An analysis based on in situ ER-2 data, *J. Geophys. Res., 94 (D9),* 11,480-11,520, 1989.

Arpag, K. H., P. V. Johnston, H. L. Miller, R. W. Sanders, and S. Solomon, Observations of the stratospheric BrO column over Colorado, 40°N, *J. Geophys. Res., 99 (D4)*, 8175-8181, 1994.

Atlas, E., S. M. Schauffler, J. T. Merrill, C. J. Hahn, B. Ridley, J. Walega, J. Greenberg, L. Heidt, and P. Zimmerman, Alkyl nitrate and selected halocarbon measurements at Mauna Loa Observatory, Hawaii, *J. Geophys. Res., 97 (D10)*, 10,331-10348, 1992.

Avallone, L. M., D. W. Toohey, S. M. Schauffler, W. H. Pollock, L. E. Heidt, E. L. Atlas, and K. R. Chan, In situ measurements of BrO during AASE II, *Geophys. Res. Lett., 22 (7)*, 831-834, 1995.

Blake, D. R., D. F. Hurst, T. W. Smith, Jr., W. J. Whipple, T.-Y. Chen, N. J. Blake, and F. S. Rowland, Summertime measurements of selected nonmethane hydrocarbons in the Arctic and subarctic during the 1988 Arctic Boundary Layer Expedition (ABLE 3A), *J. Geophys. Res., 97 (D15)*, 16,559-16,588, 1992.

Boering, K. A., S. C. Wofsy, B. C. Daube, H. R. Schneider, M. Loewenstein, J. R. Podolske, T. J. Conway, Stratospheric mean ages and transport rates from observations of carbon dioxide and nitrous oxide, *Science, 274*, 1340-1343, 1996.

Bogan, D. J., R. P. Thorn, F. L. Nesbitt, and L. J. Stief, Experimental 300K measurement of the rate constant of the reaction OH + BrO products, *J. Phys. Chem.*, *100*, 14,383-14,389, 1996.

Burkholder, J. B., R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. Vaghjiani, and A. R. Ravishankara, Atmospheric fate of CF_3Br, CF_2Br_2, CF_2ClBr, and CF_2BrCF_2Br, *J. Geophys. Res., 96 (D3)*, 5025-5043, 1991.

Butler J. H., J. W. Elkins, B. D. Hall, S. O. Cummings, and S. A. Montzka, A decrease in the growth rates of atmospheric halon concentrations, *Nature, 359*, 403-405, 1992.

Butler, J. H. and J. M. Rodriguez, Methyl bromide in the atmosphere, in *The Methyl Bromide Issue*, edited by C. H. Bell, N. Price, and B. Chakrabarti, pp. 28-90, John Wiley & Sons, New York, NY, 1996.

Butler, J. H., S. A. Montzka, A. D. Clarke, J. M. Lobert, and J. W. Elkins, Growth and distribution of halons in the atmosphere, submitted to *J. Geophys. Res.*, 1997.

Carlotti, M., et al., Measurement of stratospheric HBr using high resolution far infrared spectroscopy, *Geophys. Res. Lett., 22*, 3207-3210, 1995.

Carroll, M. A., R. W. Sanders, S. Solomon, and A. L. Schmeltekopf, Visible and near-ultraviolet spectroscopy at McMurdo Station, Antarctica 6. Observations of BrO, *J. Geophys. Res., 94 (D14)*, 16,633-16,638, 1989.

Chipperfield, M. P., D. E. Shallcross, and D. J. Lary, A model study of the potential role of the reaction BrO + OH in the production of stratospheric HBr, submitted to *Geophys. Res. Lett.*, June 1997.

Cicerone, R. J., L. E. Heidt, and W. H. Pollock, Measurements of atmospheric methyl bromide and bromoform, *J. Geophys. Res., 93 (D4)*, 3745-3749, 1988.

Class, T., R. Kohnle, and K. Ballschmiter, Chemistry of organic tracers in air VII: Bromo- and bromochloromethanes in air over the Atlantic Ocean, *Chemosphere, 15, (4)*, 429-436, 1986.

Daniel, J. S., S. M. Schauffler, W. H. Pollock, S. Solomon, A. Weaver, L. E. Heidt, R. R. Garcia, E. L. Atlas, and J. F. Vedder, On the age of stratospheric air and inorganic chlorine and bromine release, *J. Geophys. Res., 101 (D11)*, 16,757-16,770, 1996.

Danilin, M. Y. and J. C. McConnell, Stratospheric effects of bromine activation on/in sulfate aerosol, *J. Geophys. Res., 100 (D6)*, 11,237-11,243, 1995.

Danilin, M. Y., N.-D. Sze, M. K. W. Ko, J. M. Rodriguez, and M. J. Prather, Bromine-chlorine coupling in the Antarctic ozone hole, *Geophys. Res. Lett., 23 (2)*, 153-156, 1996.

DeMore, W. B., S. P. Sander, D. M Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, *Chemical kinetics and photochemical data for use in stratospheric modeling*, JPL Publication 94-26, Jet Propulsion Laboratory, Pasadena, CA, 1994.

DeMore, W. B., S. P. Sander, D. M Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, *Chemical kinetics and photochemical data for use in* *stratospheric modeling*, JPL Publication 94-26, Jet Propulsion Laboratory, Pasadena, CA, 1994.

DeMore, W. B., S. P. Sander, D. M Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, *Chemical kinetics and photochemical data for use in stratospheric modeling*, JPL Publication 97-4, Jet Propulsion Laboratory, Pasadena, CA, 1997.

Elkins, J. W., et al., *Atmospheric halocarbon records from the NOAA/CMDL flask sampling program, Trends '93: A compendium of data on global change,* ORNL/CDIAC-65, edited by T. A. Boden, D. P. Kaiser, R. J. Sepanski and F. W. Stoss, pp. 422-471, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, TN, 1993.

Elkins, J. W., et al., Airborne gas chromatograph for in situ measurements of long-lived species in the upper troposphere and lower stratosphere, *Geophys. Res. Lett., 23 (4)*, 347-350, 1996a.

Elkins, J. W. et al., Nitrous oxide and halocompounds, in *Climate Monitoring and Diagnostics Laboratory No. 23 Summary Report 1994-1995*, edited by D. J. Hofmann, J. T. Peterson, and R. M. Rosson, pp. 84-111, Environmental Research Laboratories, Boulder, CO, 1996b.

Fabian, P., R. Borchers, S. A. Penkett, and N. J. D. Prosser, Halocarbons in the stratosphere, *Nature, 294*, 733-735, 1981.

Fabian, P., R. Borchers, and K. Kourtidis, Bromine-containing source gases during EASOE, *Geophys. Res. Lett., 21 (13)*, 1219-1221, 1994.

Gao, R. S. et al., Partitioning of the reactive nitrogen reservoir in the lower stratosphere of the southern hemisphere: Observations and modeling, *J. Geophys. Res., 102 (D3),* 3935-3949, 1997.

Garcia, R. R. and S. Solomon, A new numerical model of the middle atmosphere 2. Ozone and related species, *J. Geophys. Res., 99 (D6)*, 12,937-12,951, 1994.

Geller, L. S., J. W. Elkins, J. M. Lobert, A. D. Clarke, D. F. Hurst, J. H. Butler, and R. C. Myers, Tropospheric SF_6: Observed latitudinal distribution and trends, derived emissions and interhemispheric exchange time, *Geophys. Res. Lett., 24 (6)*, 675-678, 1997.

Hall, T. M. and R. A. Plumb, Age as a diagnostic of stratospheric transport, *J. Geophys. Res., 99 (D1)*, 1059-1070, 1994.

Harnisch, J., R. Borchers, P. Fabian, and M. Maiss, Tropospheric trends for CF_4 and C_2F_6 since 1982 derived from SF_6 dated stratospheric air, *Geophys. Res. Lett., 23 (10)*, 1099-1102, 1996.

Heidt, L. E., J. F. Vedder, W. H. Pollock, R. A. Lueb, and B. E. Henry, Trace gases in the Antarctic atmosphere, *J. Geophys. Res., 94 (D9)*, 11,599-11,611, 1989.

Johnson, D. G., W. A. Traub, K. V. Chance, and K. W. Jucks, Detection of HBr and upper limit for HOBr: Bromine partitioning in the stratosphere, *Geophys. Res. Lett., 22 (11)*, 1373-1376, 1995.

Kourtidis, K., R. Borchers, and P. Fabian, Dibromomethane (CH_2Br_2) measurements at the upper troposphere and lower stratosphere, *Geophys. Res. Lett., 23 (19)*, 2581-2583, 1996.

Lal, S., R. Borchers, P. Fabian, and B. C. Krüger, Increasing abundance of $CBrClF_2$ in the atmosphere, *Nature, 316*, 135-136, 1985.

Lal, S., R. Borchers, P. Fabian, P. K. Patra, and B. H. Subbaraya, Vertical distribution of methyl bromide over Hyderabad, India, 1994, *Tellus, 46B*, 373-377, 1994.

Lary, D. J., Gas phase atmospheric bromine photochemistry, *J. Geophys. Res., 101 (D1)*, 1505-1516, 1996a.

Lary, D. J., M. P. Chipperfield, R. Toumi, and T. Lenton, Heterogeneous atmospheric bromine chemistry, *J. Geophys. Res., 101 (D1)*, 1489-1504, 1996b.

Lee, J., W. T. Sturges, S. A. Penkett, D. E. Oram, U. Schmidt, A. Engel, and R. Bauer, Observed stratospheric profiles and stratospheric lifetimes of HCFC-141b and HCFC-142b, *Geophys. Res. Lett.*, *22 (11)*, 1369-1372, 1995.

Lobert, J. M., J. H. Butler, S. A. Montzka, L. S. Geller, R. C. Myers, and J. W. Elkins, A net sink for atmospheric CH_3Br in the East Pacific Ocean, *Science, 267*, 1002-1005, 1995.

Maiss, M., L. P. Steele, R. J. Francey, P. J. Fraser, R. L. Langenfelds, N. B. A. Trivett, and I. Levin, Sulfur hexafluoride- A powerful new atmospheric tracer, *Atmos. Environ., 30 (10/11)*, 1621-1629, 1996.

McElroy, M. B., R. J. Salawitch, S. C. Wofsy, and J. A. Logan, Reductions of Antarctic ozone due to synergistic interactions of chlorine and bromine, *Nature, 321*, 759-762, 1986.

Montzka, S. A., J. H. Butler, R. C. Myers, T. M. Thompson, T. H. Swanson, A. D. Clarke, L. T. Lock, and J. W. Elkins, Decline in the tropospheric abundance of halogen from halocarbons: Implications for stratospheric ozone depletion, *Science*, *272*, 1318-1322, 1996.

Nolt, I. G., et al., Stratospheric HBr concentration profile obtained from far-infrared emission spectroscopy, *Geophys. Res. Lett., 24 (3)*, 281-284, 1997.

Osterman, G. B., R. J. Salawitch, B. Sen, G. C. Toon, R. A. Stachnik, H. M. Pickett, J. J. Margitan, J.-F. Blavier, and D. B. Peterson, Balloon-borne measurements of stratospheric radicals and their precursors: Implications for the production and loss of ozone, *Geophys. Res. Lett., 24 (9),* 1107-1110, 1997.

Penkett, S. A., B. M. R. Jones, M. J. Rycroft, and D. A. Simmons, An interhemispheric comparison of the concentrations of bromine compounds in the atmosphere, *Nature, 318*, 550-553, 1985.

Penkett, S. A., J. H. Butler, M. J. Kurylo, C. E. Reeves, J. M. Rodriguez, H. Singh, D. Toohey, R. Weiss, Methyl bromide, in *Scientific Assessment of Ozone Depletion: 1994*, pp. 10.1-10.26, World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 37, 1995.

Podolske, J., and M. Loewenstein, Airborne tunable diode laser spectrometer for trace gas measurement in the lower stratosphere, *Appl. Opt., 32*, 5324-5333, 1993.

Pundt, I., J.-P. Pommereau, and F. Lefèvre, Investigation of stratospheric bromine and iodine oxides using the SAOZ balloon sonde, in Proceedings of the Quadriennial Ozone Symposium, 1996.

Ravishankara, A. R., S. Solomon, A. A. Turnipseed, and R. F. Warren, Atmospheric lifetimes of long-lived halogenated species, *Science, 259*, 194-199, 1993.

Salawitch, R. J., S. C. Wofsy, and M. B. McElroy, Chemistry of OClO in the Antarctic stratosphere: Implications for bromine, *Planet. Space Sci., 36 (2)*, 213-224, 1988.

Salawitch, R. J., et al., Chemical loss of ozone in the Arctic polar vortex in the winter of 1991-1992, *Science, 261*, 1146-1149, 1993.

Salawitch, R. J., et al., The distribution of hydrogen, nitrogen, and chlorine radicals in the lower stratosphere: Implications for changes in O_3 due to emission of NO_y from supersonic aircraft, *Geophys. Res. Lett., 21 (23)*, 2547-2550, 1994.

Sanhueza, E., P. J. Fraser, R. J. Zander, Source gases: Trends and budgets, in *Scientific Assessment of Ozone Depletion: 1994*, pp. 2.1-2.38, World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 37, 1995.

Schauffler, S. M., L. E. Heidt, W. H. Pollock, T. M. Gilpin, J. F. Vedder, S. Solomon, R. A. Lueb, and E. L. Atlas, Measurements of halogenated organic compounds near the tropical tropopause, *Geophys. Res. Lett.*, *20 (22)*, 2567-2570, 1993.

Schmidt U., G. Kulessa, E. Klein, E.-P. Roth, P. Fabian, and R. Borchers, Intercomparison of balloon-borne cryogenic whole air samplers during the MAP/GLOBUS 1983 campaign, *Planet. Space Sci., 35 (5),* 647-656, 1987.

Singh, O. N., R. Borchers, P. Fabian, S. Lal, and B. H. Subbaraya, Measurements of atmospheric BrO_x radicals in the tropical and mid-latitude atmosphere, *Nature, 334*, 593-595, 1988.

Singh, H. B., Halogens in the atmospheric environment, in *Composition, Chemistry, and Climate of the Atmosphere*, edited by H. B. Singh, pp. 216-250, Van Nostrand Reinhold, New York, NY, 1995.

Solomon, S., R. W. Sanders, M. A. Carroll, and A. L. Schmeltekopf, Visible and near-ultraviolet spectroscopy at McMurdo Station, Antarctica 5. Observations of the diurnal variations of BrO and OClO, *J. Geophys. Res., 94 (D9)*, 11,393-11403, 1989.

Solomon, S., D. Wuebbles, I. Isaksen, J. Kiehl, M. Lal, P. Simon, and N.-D. Sze, Ozone depletion potentials, global warming potentials, and future chlorine/bromine loading, in *Scientific Assessment of Ozone Depletion: 1994*, pp.13.1-13.36, World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 37, 1995.

Sturges, W. T., Halocarbons in the Arctic and Antarctic atmosphere, in *The Tropospheric Chemistry of Ozone in the Polar Regions*, edited by H. Niki and K. H. Becker, pp. 117-130, Springer-Verlag, New York, 1993.

Toohey, D. W., J. G. Anderson, W. H. Brune, and K. R. Chan, In situ measurements of BrO in the Arctic stratosphere, *Geophys. Res. Lett., 17 (4)*, 513-516, 1990.

United Nations Environmental Program (UNEP), Report of the Seventh Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer, UNEP World Meteorological Organization (WMO), Geneva, December 1995.

Volk, C. M., J. W. Elkins, D. W. Fahey, G. S. Dutton, J. M. Gilligan, M. Loewenstein, J. R. Podolske, K. R. Chan, and M. R. Gunson, On the evaluation of source gas lifetimes from stratospheric observations, *J. Geophys. Res.*, in press.

Wahner, A., J. Callies, H.-P. Dorn, U. Platt, and C. Schiller, Near UV atmospheric absorption measurements of column abundances during Airborne Arctic Stratospheric Expedition, January-February 1989: 3. BrO observations, *Geophys. Res. Lett., 17 (4)*, 517-520, 1990.

Weisenstein, D. K., M. K. W. Ko, N.-D. Sze, and J. M. Rodriguez, Potential impact of SO_2 emissions from stratospheric aircraft on ozone, *Geophys. Res. Lett., 23 (2)*, 161-164, 1996.
Wennberg, P. O., et al., Removal of stratospheric O_3 by radicals: In situ measurements of OH, HO_2, NO, NO_2, ClO, and BrO, *Science, 266*, 398-404, 1994.

Wennberg, P. O., J. W. Brault, T. F. Hanisco, R. J. Salawitch, and G. H. Mount, The atmospheric column abundance of IO: Implications for stratospheric ozone, *J. Geophys. Res.*, *102 (D7)*, 8887-8898, 1997.

Woodbridge, E. L., et al., Estimates of total organic and inorganic chlorine in the lower stratosphere from in situ and flask measurements during AASE II, *J. Geophys. Res., 100 (D2*), 3057-3064, 1995.

Yung, Y. L., J. P. Pinto, R. T. Watson, and S. P. Sander, Atmospheric bromine and ozone perturbations in the lower stratosphere, *J. Atmos. Sci., 37*, 339-353, 1980.

Yvon, S. A. and J. H. Butler, An improved estimate of the oceanic lifetime of atmospheric CH_3Br, *Geophys. Res. Lett., 23 (1)*, 53-56, 1996.

Figure Legends

Figure 1. Altitude profile and calculated mean age of air for the flight of October 10, 1994. The flight profile shown in this figure is typical of the flight patterns flown during ASHOE/MAESA in which the majority of the flight time occurred in the stratosphere. The large majority of each flight occurred in the stratosphere. (The tropopause is at 8-10 km.) Altitude profiles were obtained on ascent, descent, and during a dive executed in the middle of the flight. The mean age of air along the flight path was calculated from the measured mixing ratios of the age tracer, SF_6.

Figure 2. Recent record of long-lived organic bromine species at Earth's surface. The mixing ratios of CH_3Br, CH_2Br_2, and CH_2BrCl were assumed to be constant from 1988 to 1996. The halon mixing ratios were obtained from the NOAA/CMDL flask measurement program.

Figure 3. Normalized data sets and resulting correlations for the six organic bromine species included in our calculation. Normalization constants for each individual set of data are given in Table 4. The solid curves are the best fits to the data using the equation $[X]/[X]_o = ([CFC\text{-}11]/[CFC\text{-}11]_o)^{1/d}$ where the subscript, o, represents the October 1994 surface mixing ratios. The October 1994 surface mixing ratio for each molecule is given in parentheses. ACATS-IV data are shown in black circles, NCAR data in blue triangles, UEA data in green diamonds, and UC-Irvine data in red squares. The dashed curves are fits to the AER model results matched for season and location with the NCAR data. There is good agreement between the measured and modeled correlations. The value of d for the modeled H-1211 correlation is 0.59 which makes it difficult to distinguish from the measured correlation.

Figure 4. Correlation between CBr_y and CFC-11 in the stratosphere. The triangles represent the correlation from the summation of correlations for all source molecules (equation (14)). The solid curve is the best fit to the correlation using a power law function with power coefficient 1/d (d = 0.53) . The "effective lifetime" of CBr_y is estimated to be approximately one half that of CFC-11.

Figure 5. ACATS-IV measurements of H-1211 (dry mole fraction) as a function of altitude and latitude during ASHOE/MAESA. The largest mixing ratios were observed in the tropics consistent with upwelling of tropospheric air in the tropics. The smaller mixing ratios observed at high latitudes were associated with larger mean ages (Figure 6). The lower values of [H-1211] observed in air parcels with older mean ages is largely the result of photolysis. In addition, older air parcels entered the stratosphere with less H-1211 than younger air parcels because [H-1211] has been increasing in the troposphere. The dashed curves in the figure represent the location of the tropopause as defined by a potential temperature of 380K.

Figure 6. Calculated values of mean age as a function of altitude and latitude during ASHOE/MAESA based upon ACATS-IV measurements of SF_6. The air parcels with the smallest mean ages were located in the tropical upwelling region. Descent of older air at high latitudes was observed in both the northern and southern hemispheres. The dashed curves in the figure represent the location of the tropopause as defined by a potential temperature of 380K.

Figure 7. Calculated results for $[Br_{Total}]$ (triangles), and its partitioning into organic, CBr_y (circles), and inorganic, Br_y (squares), constituents. The dashed curves represent one standard deviation windows calculated from the uncertainties listed in Tables 2 and 3.

Figure 8. Calculated mixing ratios of Br_y as a function of CFC-11 using the organic bromine method described in this work (gray squares), the inorganic bromine method (black triangles), and an earlier result using the organic bromine method (solid curve).

Table 1. Bromine containing compounds that have been measured at Earth's surface.

Molecule	Formula	Source[a]	Mixing Ratios (ppt)	Atmospheric Lifetime (y)	ODP
			Sources of Stratospheric Bromine		
Methyl Bromide	CH_3Br	A, N	11[b]	0.8[c]	0.43[d]
Halon-1211	$CBrClF_2$	A	2.5[e]	20[f]	5[f]
Halon-1301	$CBrF_3$	A	2.0[e]	65[f]	13[f]
Halon-2402	$CBrF_2CBrF_2$	A	0.47[g]	<20[h]	~5[i]
Dibromomethane	CH_2Br_2	N	1.4-3.7[a,j]	<1, 0.2[d,k]	
Bromochloromethane	CH_2BrCl	N	0.5-2.9[a]	<1	
			Negligible Sources of Stratospheric Bromine		
Bromoform	$CHBr_3$	A, N	0-10[l,m,n]	<0.083, 0.03-0.1[d,k]	
Dibromochloromethane	$CHBr_2Cl$	N	<1[a]	0.4[k]	
Bromodichloromethane	$CHBrCl_2$	N	0.6-3.8[a]	0.4[k]	
1,2-dibromoethane	CH_2BrCH_2Br	A	0-17.7[a]	0.4[k]	

Compounds in the upper portion of the table have atmospheric lifetimes long enough to allow their transport into the stratosphere. Compounds in the lower portion of the table have short atmospheric lifetimes and are assumed to contribute negligible amounts of bromine to the stratosphere.
[a] *Sturges* [1993], sources are anthropogenic (A) or natural (N).
[b] *Penkett, et al.* [1995]
[c] *Yvon and Butler* [1996]
[d] *Butler and Rodriguez* [1996]
[e] *Sanhueza et al.* [1995]
[f] *Solomon et al.* [1995]
[g] *S. Montzka*, unpublished data from the NOAA/CMDL flask network [1995]
[h] *Burkholder et al.* [1991]
[i] Estimated from the ODP of H-1301 by substitution of the lifetime, molecular weight, and number of bromine atoms/molecule of H-2402 for those of H-1301.
[j] *Schauffler et al.* [1993]
[k] *Singh* [1995]
[l] *Cicerone et al.* [1988]
[m] *Atlas et al.* [1992]
[n] *Penkett et al.* [1985]

Table 2. Fit parameters and uncertainties describing the time dependence of the surface mixing ratios of long-lived organic bromine species from 1988 to 1995.

Molecule	# of Br atoms per molecule	Mixing Ratio, [X(t)] $[X(t)] = a + b(t - 1994.875) + c(t - 1994.875)^2$		
		a	b	c
Methyl Bromide	1	9.8 ±0.6	0.0 ±0.2	0.0 ±0.0
Halon-1211	1	3.15 ±0.20	0.151 ±0.017	-0.0036 ±0.0043
Halon-1301	1	2.25 ±0.13	0.115 ±0.010	-0.0055 ±0.0023
Halon-2402	2	0.47 ±0.03	0.010 ±0.004	0.0 ±0.0
Dibromomethane	2	1.1 ±0.2	0.0 ±0.1	0.0 ±0.0
Bromochloromethane	1	0.14 ±0.03	0.00 ±0.01	0.0 ±0.0

We have assumed that the mixing ratios of the naturally occurring species were constant from 1988 to 1995. We allowed for changes in the mixing ratios by including uncertainty in the linear growth coefficient. The time series of halon mixing ratios at Earth's surface come from flask measurements collected at NOAA/CMDL's seven baseline monitoring stations. The trends for H-1211 and H-1301 are based on measurements that began in mid-1989. The trend for H-2402 is based on measurements that began in 1995 and archived air samples. The mixing ratio as a function of time, [X(t)], is given by the equation, $[X(t)] = a + b(t - 1994.875) + c(t - 1994.875)^2$. We have chosen mid-October 1994 as our reference time because this coincides with the in situ stratospheric measurements taken during the ASHOE/MAESA mission. With this convention, the constant term, a, is the surface mixing ratio for mid-October 1994.

Table 3. Accuracy and precision of the CFC-11, SF_6, and H-1211 measurements from ACATS-IV during ASHOE/MAESA.

Molecule	Accuracy	Precision
CFC-11	±5 ppt	±1 ppt
SF_6	±0.5 ppt	±0.04 ppt
H-1211	±0.2 ppt	± 0.05 ppt

Table 4. Correlations of long-lived species of organic bromine with CFC-11.

Molecule	Source (Mission)	$[X]_o$ (ppt)	d
CH_3Br	UC-Irvine (AASE)	12.1	0.67 ±0.01
	NCAR (STRAT)	10.2	
H-1211	UC-Irvine (AASE)	2.9	0.600 ±0.003
	UEA/KFA	1.8	
	CMDL (ASHOE/MAESA)	3.2	
	NCAR (STRAT)	3.5	
H-1301	UC-Irvine (AASE)	2.0	0.98 ±0.01
	UEA/KFA	1.1	
	NCAR (STRAT)	2.2	
H-2402	UEA/KFA	0.3	0.65 ±0.12
	NCAR (STRAT)	0.4	
CH_2Br_2	UEA/KFA (3 flights)	0.8	0.12 ±0.03
	NCAR (STRAT)	1.1	
CH_2BrCl	UEA/KFA (1 flight)	1.1	0.16 ±0.03
	NCAR (STRAT)	0.14	
CFC-11	UC-Irvine (AASE)	270.0	
	UEA/KFA	261.0	
	CMDL (ASHOE/MAESA)	271.0	
	NCAR (STRAT)	276.3	

Stratospheric measurements of the compounds that contribute to stratospheric bromine from four research groups were used to obtain a correlation between the mixing ratios of each brominated compound and the mixing ratio of CFC-11. To compensate for the different calibration scales used by each research group, he data from different research groups was normalized so that each species had a normalized value of one at the tropopause. The UEA/KFA data consists of data from balloon flights on March 15, 1993, September 20, 1993, January 1, 1994, and July 10, 1994. UEA/KFA flights were normalized individually. The UEA/KFA flights occurred at 44˚N except for the flight of January 1, 1994 which occurred at 68˚N. The other data were taken from samplers flown aboard aircraft. The form of the parameterization is $([X]/[X]_o) = ([CFC\text{-}11]/[CFC\text{-}11]_o)^{(1/d)}$. The subscript, o, designates the tropospheric mixing ratio measured by each group. No correction was applied to account for changes in the mixing ratios at Earth's surface over the measurement time period or different sampling locations. Though there are differences in the absolute mixing ratios measured by each laboratory there is qualitative agreement among the normalized data sets (Figure 3).

Table 5. Comparison of calculated results for Br_y/Br_{Total} and Cl_y/Cl_{Total} in stratospheric air.

Study	Data Set	Basis for the Age Calculation	Calc. Age	$\frac{Br_y}{Br_{Total}}$	$\frac{Cl_y}{Cl_{Total}}$	N_2O
Woodbridge et al. 1995	AASE II	CO_2	5 y	-	87.5%	100 ppb
Daniel et al. 1996	AASE II	CO_2/CFC-115	5-6 y	90%	85%	100 ppb
This Work	ASHOE /MAESA	SF_6	6 y	97.5%	-	130 ppb

The mixing ratio of N_2O associated with the calculated fractions of inorganic chlorine and bromine has been included as a reference point for the mean age of the sampled air independent of the method used to determine the mean age of the air.