

OH reaction rate constant, IR absorption spectrum, ozone depletion potentials and global warming potentials of 2-bromo-3,3,3-trifluoropropene

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[1] The rate constant for the gas phase reaction of OH radicals with BTP (2-bromo-3,3,3-trifluoropropene, $\text{CH}_2 = \text{CBrCF}_3$) was measured using a flash photolysis resonance-fluorescence technique over the temperature range 220 K to 370 K. The Arrhenius plot was found to exhibit noticeable curvature. The temperature dependence of the rate constant can be represented as $k_{\text{BTP}}(220 - 370 \text{ K}) = 4.85 \times 10^{-13} \times (T/298)^{0.92} \times \exp\{+613/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For atmospheric modeling purposes, $k_{\text{BTP}}(T)$ can be equally well represented by the standard Arrhenius expression $k_{\text{BTP}}(220 - 298 \text{ K}) = 1.05 \times 10^{-12} \times \exp\{+381/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The IR absorption cross-sections of BTP were also measured between 450 cm^{-1} and 1900 cm^{-1} . BTP atmospheric lifetime, Ozone Depletion Potential (ODP), and Global Warming Potential (GWP) were evaluated in the Whole Atmosphere Community Climate Model for land emissions from 30 to 60°N and from 60°S to 60°N . The global, annual average atmospheric lifetime of BTP in the former scenario was 7.0 days, its ODP was 0.0028, and its GWP (100-yr time horizon) was 0.0050; in the latter scenario, the global, annual average BTP lifetime was 4.3 days, ODP was 0.0052, and 100-yr GWP was 0.0028. The short lifetime, low ODP, and low GWP indicate that BTP should have minimal effects on ozone and climate. Little BTP reaches the stratosphere in either emission scenario, but 27% of the ozone loss in the 30 to 60°N scenario and 46% of the ozone loss in the 60°S to 60°N scenario occurs above the tropopause due to Br_y from BTP.

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1. Introduction

[2] Since the recognition of adverse environmental effects from the long-lived, fully halogenated gases such as the chlorofluorocarbons (CFCs) and Halons, industry has sought replacement compounds for those gases that perform their functions, but lack adverse ozone or climate effects. The primary approach to this problem has been to test candidate replacement compounds that have short atmospheric lifetimes and lack chlorine or bromine, the halogen atoms that catalyze ozone destruction.

[3] One recently proposed candidate as a possible substitute for Halons in handheld fire extinguishers used in the presence of people in confined spaces such as aircraft cabins is 2-bromo-3,3,3-trifluoropropene (BTP, also named 2-bromo-

3,3,3-trifluoropropylene, chemical formula $\text{CH}_2 = \text{CBrCF}_3$). The efficiency of bromine at catalyzing ozone destruction, because of the ease in which bromine atom and bromine oxide are regenerated from bromine reservoir species, results in Ozone Depletion Potential (ODP) values for many brominated compounds that are unacceptably high. The presence of a carbon-carbon double bond is expected to render BTP highly reactive toward the hydroxyl radical (OH) in the troposphere, so that relatively little BTP should reach the stratosphere to impact stratospheric ozone.

[4] The reaction rate constant with OH, $k_{\text{BTP}}(T)$, for temperatures between 250 and 370 K and the UV absorption cross sections for BTP between 164 and 253 nm have been measured by Orkin *et al.* [2002]. The BTP atmospheric lifetime was estimated from the OH rate constant expression by the method of Spivakovsky *et al.* [2000] as 2.8 days. The Orkin *et al.* [2002] rate constant $k_{\text{BTP}}(T)$ was later used by Brioude *et al.* [2010] in a calculation of BTP atmospheric lifetime and ODP using the FLEXPART Lagrangian model. Brioude *et al.* obtained BTP lifetimes ranging from 3.1 days for emissions originating in the Indian subcontinent to 7.1 days for emissions originating in Europe, and reported

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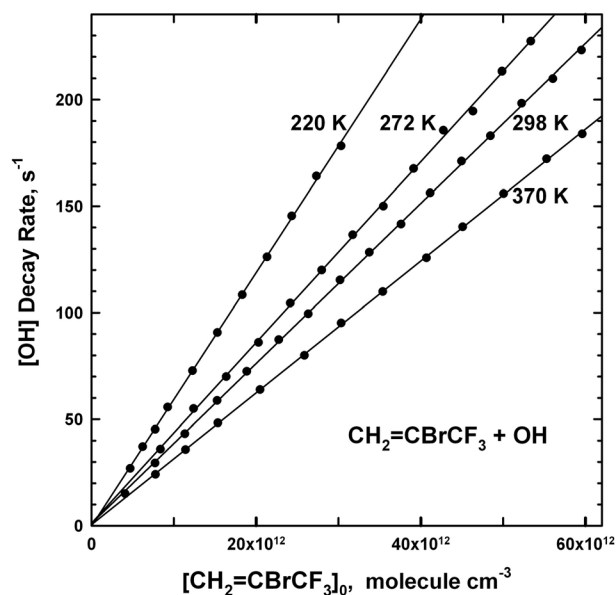


Figure 1. OH decay rates due to reaction with $\text{CH}_2 = \text{CBrCF}_3$ versus the reactant concentrations at 220 K, 272 K, 298 K, and 370 K.

annually averaged ODPs ranging from 0.0013 for European emissions to 0.044 for emissions from the Indian subcontinent in Brioude *et al.*'s [2010] auxiliary material.

[5] The fast reaction with OH radicals in the troposphere is likely to be the major removal process for BTP in the atmosphere which dictates its residence time and, therefore, potential environmental impacts. Therefore, we re-visited this reaction using our recently improved apparatus to provide more accurate kinetic data over the atmospheric temperatures to be used in the following detailed modeling. We also measured IR absorption cross sections of BTP to provide a basis for GWP estimations. Then, we obtain the atmospheric lifetime and ODP using the Whole Atmosphere Community Climate Model (WACCM) for two scenarios of BTP emissions from land surfaces. The first, representing the most likely region of initial use, is from all land surfaces at latitudes 30°N to 60°N. The second scenario is from all land surfaces at latitudes 60°S to 60°N, similar to the “global” emissions used for many past ODP studies on short-lived source gases such as *n*-propyl bromide [Wuebbles *et al.*, 2001; Ko *et al.*, 2003; Wuebbles *et al.*, 2011]. The WACCM results are also used with our radiative transfer model to derive estimates of Global Warming Potentials (GWPs) for BTP in those scenarios.

2. Experimental Section

2.1. OH Reaction Rate Constant Measurements

[6] General descriptions of the apparatus and the experimental method used to measure the OH reaction rate constants are given in previous papers [Kurylo *et al.*, 1982; Orkin *et al.*, 1996]. In the present work we used the same principal configuration of the apparatus with a number of modifications made to improve the accuracy of the obtained kinetic data by decreasing and quantifying the instrumental uncertainties. In particular, the gas handling system was completely replaced and a new reaction cell and photomultiplier

were used. Modifications to the apparatus and the measurement procedure were recently described in detail [Orkin *et al.*, 2010, 2011]. The reaction was studied in a double-walled Pyrex reactor equipped with quartz windows by using a flash photolysis-resonance fluorescence technique. The reactor temperature is controlled with methanol or water circulated between the outer walls. The reaction was studied in argon carrier gas at total pressure of 4.00 kPa (30.0 Torr). Flows of dry argon, argon bubbled through water temperature-controlled at 276 K, and a mixture of BTP diluted with Ar flowed through the reactor at a total flow rate of $1.3 \text{ cm}^3 \text{ s}^{-1}$, STP. The BTP/Ar mixtures were prepared in 5 L glass bulbs equipped with Teflon/glass valves. The concentrations of the gases in the reactor were determined by measuring the gas flow rates and the total pressure with MKS Baratron manometers. Flow rates of argon, $\text{H}_2\text{O}/\text{Ar}$ mixture, and the reactant/argon mixture were measured and maintained using MKS mass flow controllers directly calibrated for every gas mixture. Hydroxyl radicals were produced by the pulsed flash photolysis of H_2O and monitored by their resonance fluorescence near 308 nm as described in detail in earlier publications. The procedure for deriving the reaction rate constant from such data has been described by Orkin *et al.* [1996, 2010]. Figure 1 gives examples of the derived OH decay rates due to reaction with $\text{CH}_2 = \text{CBrCF}_3$ plotted versus the reactant concentrations at various temperatures. At each temperature the rate constant was determined from a fit to all of the decay rates obtained at that temperature (i.e., the slope of a plot similar to those shown in Figure 1). The temperatures for the measurements were chosen to be approximately equally distant along the Arrhenius $1/T$ scale so that they would be equally weighted in the fitting procedure. The accuracy of kinetic data was analyzed in detail by Orkin *et al.* [2010, 2011].

2.2. IR Absorption Cross-Sections Measurements

[7] The IR absorption spectrum was measured by using a Nicolet 6700 FTIR spectrophotometer with spectral resolutions of 0.125 cm^{-1} and 0.25 cm^{-1} (recorded with a step of 0.06 cm^{-1} and 0.12 cm^{-1} , respectively). A $(10.2 \pm 0.05) \text{ cm}$ glass absorption cell fitted with KBr windows was fixed in the spectrophotometer to minimize a baseline shift due to changes in the absorption cell position. The temperature of the cell was measured to be $(295 \pm 1) \text{ K}$. Absorption spectra of the evacuated cell and of the cell filled with a gas sample were alternately recorded several times, and the absorption cross sections at the wave number $\nu \text{ (cm}^{-1}\text{)}$ were calculated. Details and potential complications of these measurements are discussed by Orkin *et al.* [2010]. The overall instrumental uncertainty associated with the optical path length, pressure measurements, and temperature stability was estimated to be less than 1%.

2.3. Materials

[8] The sample of 2-bromo-3,3,3-trifluoropropene was obtained from SynQuest Laboratories, Inc., and it was degassed through multiple freeze-pump-thaw-boil cycles. The bulk liquid sample had a stated purity of $\sim 99\%$ with $\sim 0.5\%$ of 1,2-dibromo-3,3,3-trifluoropropane ($\text{CH}_2\text{BrCHBrCF}_3$) and $\sim 0.2\%$ of 1-bromo-3,3,3-trifluoroacetone ($\text{CH}_2\text{BrC(O)CF}_3$) being the main impurities. The concentration of these lower volatility compounds in the vapor phase was substantially

Table 1. Rate Constants Measured in the Present Work for the Reaction of OH With CH₂ = CBrCF₃^a

T, K	$k_{BTP}(T) \times 10^{12}$ (cm ³ molecule ⁻¹ s ⁻¹)	[CH ₂ = CBrCF ₃] (10 ¹³ molecule/cm ³)	Test Experiment Conditions
220	5.96 ± 0.04 (30)	0.47–3.63	
230	5.48 ± 0.06 (21)	0.56–4.49	
240	5.13 ± 0.06 (9)	0.62–4.49	
250	4.80 ± 0.04 (17)	0.56–4.49	
260	4.56 ± 0.03 (16)	0.62–5.22	
272	4.27 ± 0.05 (17)	0.78–6.01	
	<i>4.26 ± 0.06 (15)</i>	<i>0.84–5.34</i>	Pressure: 0.93 kPa (7 Torr)
285	3.98 ± 0.02 (9)	0.78–6.00	
298	3.79 ± 0.02 (35)	0.41–5.95	
	<i>3.76 ± 0.04 (8)</i>	<i>0.77–5.93</i>	[OH] ₀ : 50%
	<i>3.75 ± 0.03 (8)</i>	<i>0.77–5.93</i>	Flash Energy: 200%
	<i>3.79 ± 0.06 (8)</i>	<i>1.10–6.37</i>	[OH] ₀ : 200%
	<i>3.86 ± 0.03 (8)</i>	<i>0.58–5.34</i>	[OH] ₀ : 400%, Flash Energy: 200%
313	3.61 ± 0.02 (17)	0.77–5.96	
330	3.40 ± 0.04 (18)	0.77–5.97	
350	3.24 ± 0.04 (9)	0.77–5.94	
370	3.11 ± 0.02 (28)	0.77–5.96	

^aThe uncertainties are two Standard Errors from the least squares fit of a straight line to the measured OH decay rates versus the reactant concentrations. When estimates for instrumental uncertainties are added, the overall uncertainty of the rate constant (95% confidence limit) is estimated to be ~2% increasing to 2.5% at lowest temperatures. The boldfaced data are results of the fit to all measurements performed at the particular temperature and 4.00 kPa (30.0 Torr) total pressure using a 0.25% mixture. These data are shown in Figure 1 and were used to derive the temperature dependences. The italicized data are results of some test experiments. The number of experiments for each temperature is included in parentheses.

smaller (0.02% to 0.05%) resulting in ~99.8% purity of the vapor phase, which was used to prepare mixtures for OH reaction rate constant measurements. A few smaller low-volatile impurities were detected in the liquid phase by a GC-FID analysis. The concentration of these impurities in the vapor phase was also substantially smaller than in the liquid phase. The vapor phase was enriched with the more volatile olefinic impurity, 3,3,3-trifluoropropene (up to ~0.06% compared to less than ~0.006% in the liquid phase) and a small amount of 1,1,1-trifluoroacetone (~0.002%). We used 99.9999% purity argon (Spectra Gases Inc.) as a carrier gas.

3. Experimental Results

3.1. OH Reaction Rate Constant

[9] The rate constants determined for this reaction at various temperatures are presented in Table 1. The bold-highlighted data result from fits to all measurements performed at the indicated temperature under our “standard” conditions: 4.00 kPa (30.0 Torr) total pressure, ~6 × 10¹⁴ molecule/cm³ of H₂O in the reactor. These data are shown in Figure 2 with filled circles.

[10] To check for any complications, test experiments were performed with variations of H₂O concentration, flash energy, and the total pressure in the reactor. The experiments were done to check for a possible influence of the secondary radical or photolysis product reactions on the measured rate constant. Some results of test experiments (italicized) are shown in Table 1. No statistically significant changes of the measured reaction rate constant were observed in these experiments. Note that the title reaction occurs via addition of OH to an

unsaturated C atom. Therefore, in spite of the multiatomic nature of the BTP molecule there is a possibility that the reaction is pressure dependent. The test experiments revealed no indication of any variation in the measured rate constants when pressure was changed.

[11] The Arrhenius plot in Figure 2 exhibits a curvature that is clearly resolved in our experiments. Our three-parameter modified Arrhenius expression fit to the data set from Table 1, as shown in Figure 2, is:

$$k_{BTP}(220-370\text{ K}) = 4.85 \times 10^{-13} \times (T/298)^{0.92} \times \exp\{+613/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (1)$$

A goodness of the fit cannot be seen in the Arrhenius plot. Therefore, Figure 2 (bottom) shows the experimental data reported in Table 1 normalized by this expression (1) with error bars representing the relative errors of measurements from Table 1 (filled circles). For atmospheric modeling purposes, $k_{BTP}(T)$ below room temperatures can be represented by the standard Arrhenius expression obtained from the fit to the data between 220 K and 298 K

$$k_{BTP}(220-298\text{ K}) = (1.05 \pm 0.04) \times 10^{-12} \times \exp\{+(381 \pm 10)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (2)$$

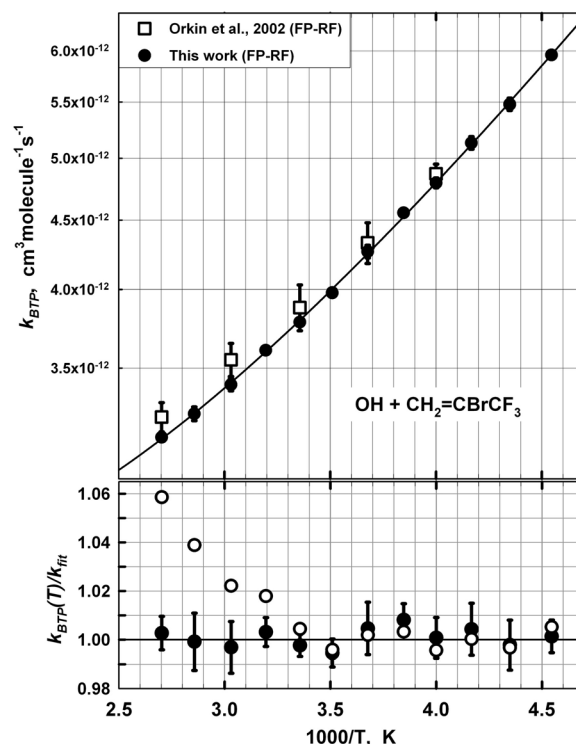


Figure 2. (top) The results of rate constant measurements for the reaction between OH and CH₂ = CBrCF₃, $k_{BTP}(T)$: squares, Orkin *et al.* [2002]; circles, this study. The solid line shows a three-parameter fit to the data from this study given by expression (1). (bottom) The ratio of rate constants measured in this study to those calculated from the three-parameter temperature dependence (1) (solid circles) and from the two-parameter Arrhenius dependence (2) (open circles).

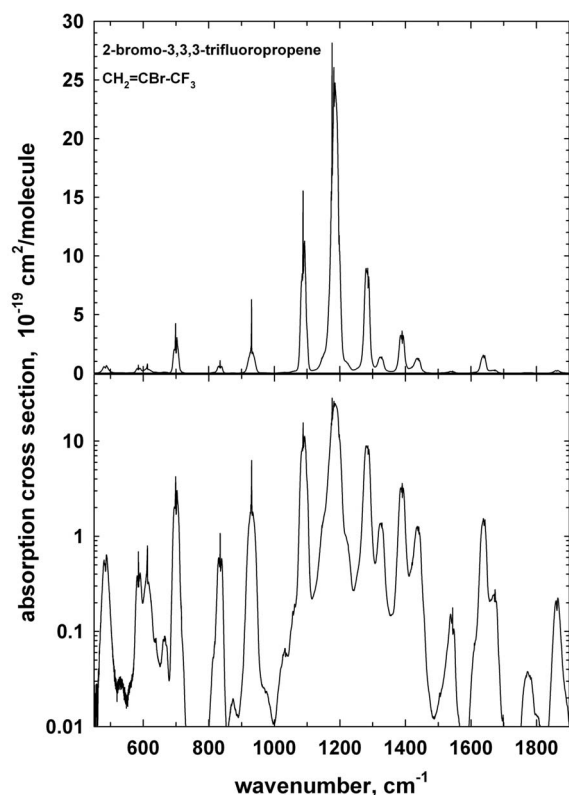


Figure 3. IR absorption spectrum of BTP obtained with a spectral resolution of 0.25 cm^{-1} .

[12] The experimental data normalized by expression (2) are shown in Figure 2 (bottom) with open circles. Their relative errors are the same as shown for the corresponding filled circles; they are omitted to not overload Figure 2. One can see that the rate constants measured at below room temperatures deviate from the recommended expression (2) by less than 0.5%. However, expression (2) underestimates the rate constant above room temperature.

[13] The presence of reactive impurities is a potential source for overestimating the measured reaction rate constant. However, in our case the detected impurities are less reactive toward OH than the target compound, $\text{CH}_2 = \text{CBrCF}_3$. The rate constant of the reaction between OH and $\text{CH}_2 = \text{CHCF}_3$ is smaller than k_{BTP} determined in this study by more than a factor of 2 [Orkin *et al.*, 1997] and, therefore, the presence of this impurity in the amount of less than 0.1% cannot contribute to the measured rate constant. There are no available data on the reactivity of either $\text{CH}_2\text{BrCHBrCF}_3$ or $\text{CH}_2\text{BrC(O)CF}_3$ toward OH. However, the OH reaction rate constants of similar molecules, $\text{CH}_3\text{CH}_2\text{CF}_3$ and $\text{CH}_3\text{C(O)CF}_3$, are much smaller than k_{BTP} measured in this study. The difference is as large as more than a factor of 60 for $\text{CH}_3\text{CH}_2\text{CF}_3$ [Rajakumar *et al.*, 2006] and more than a factor of 500 for $\text{CH}_3\text{C(O)CF}_3$ [Carr *et al.*, 2003], respectively at room temperature and increasing at lower temperatures. Also, the test experiments were done to compare the results obtained with mixtures prepared from the vapor phase and liquid phase of the BTP sample, which have substantially different amounts of impurities. The OH reaction rate constants measured with these two

mixtures were statistically indistinguishable with the difference of less than 1%. Thus we are confident that the results of our measurements are not affected by the presence of impurities in the sample.

[14] Results of the only available set of measurements of $k_{\text{BTP}}(T)$ are shown in Figure 2 with open squares. These data exceed the prediction of expression (1) by less than 4% and therefore coincide with results of this work within the combined uncertainty. The reported total uncertainty of these older data was estimated to be ca. 6%. The detailed analysis of uncertainties presented by Orkin *et al.* [2010] allows us to estimate the total instrumental uncertainty of the reaction rate constant measured in the present study to be as small as 2% (room temperature and above) to 2.5% (at lowest measurement temperatures). Based on the available kinetic data we can conclude that impurities found in the BTP sample are less reactive toward OH than the main compound. Therefore, an additional uncertainty of the measured rate constant due to the presence of impurities should not exceed 1%. Although both available data sets for the title reaction were obtained in the same laboratory, the apparatus was completely rebuilt between these studies. Also, different samples of BTP were used in these two studies with the particular attention to their purity and the nature of the impurities. Thus we can conclude that the rate constant of the reaction between OH and BTP is well established.

3.2. IR Absorption Spectra

[15] The IR absorption spectrum of BTP between 450 cm^{-1} and 1900 cm^{-1} is shown in Figure 3. The spectrum was combined from the results of measurements at various pressures of BTP between 0.13 kPa to 27 kPa (1 Torr to 200 Torr). Figure 3 (top) illustrates the main absorption bands while Figure 3 (bottom) shows the same spectrum in log scale to illustrate smaller absorption features. IR absorption cross sections of BTP are available in the auxiliary material.¹

[16] Further experiments were performed with spectral resolution of 0.125 cm^{-1} and with $\text{CH}_2 = \text{CBrCF}_3$ pressurized with nitrogen bath gas to test the adequacy of the IR spectrum presented in Figure 3 for atmospheric applications. The presence of either 44.4 kPa (333 Torr) or 88.4 kPa (666 Torr) of nitrogen bath gas changes the integrated intensities of main absorption bands located near 1280 cm^{-1} , 1185 cm^{-1} , and 1090 cm^{-1} by less than 1%. The spectral resolution of 0.125 cm^{-1} does not affect the integrated band intensities either. Only small narrow absorption peaks (1176.5 cm^{-1} , 1088.0 cm^{-1} , and 930.9 cm^{-1}) at the top of the wide absorption bands have been slightly affected (3% to 12%) by the spectral resolution and the presence of bath gas. However, these absorption features are very small (0.2% to 0.5%) compared to the integrated absorption by BTP.

4. Atmospheric Effects of BTP

4.1. Atmospheric Chemistry-Climate Model

[17] WACCM version 3.5.48, as used in this study and by investigators at the National Center for Atmospheric Research

¹Auxiliary material data sets are available at <ftp://ftp.agu.org/apend/jd/2011jd016518>. Other auxiliary material files are in the HTML. doi:10.1029/2011JD016518.

for the SPARC (Stratospheric Processes and their Role in Climate) 2010 Report on the Evaluation of Chemistry-Climate Models [Eyring *et al.*, 2010], represents the Earth's atmosphere from the surface to the lower thermosphere (4.5×10^{-6} mbar, or roughly 145 km) at a resolution of 2.5° in longitude by 1.9° in latitude. This three-dimensional chemistry-climate model is run in offline mode for this study, in which temperature, winds, specific humidity, and other meteorological fields are supplied by a previous run of WACCM 3.5 representing the year 2000 (R. Garcia, private communication, 2007). WACCM 3.5.48 includes 125 species, of which 15 are relevant mostly to thermospheric processes, and uses the JPL06 chemistry recommendation [Sander *et al.*, 2006] extended for non-methane hydrocarbon chemistry to best represent tropospheric oxidative capacity in a similar way to the tropospheric chemistry in the Model for Ozone and Related Tracers (MOZART) version 3 [Kinnison *et al.*, 2007] and version 4 [Emmons *et al.*, 2010]. The WACCM lightning NO_x yield has been scaled globally to produce an annual total NO_x of 5.0 TgN, consistent with the recommendation of Schumann and Huntrieser [2007]. Wet deposition is also based on the MOZART 3 approach [Kinnison *et al.*, 2007; Horowitz *et al.*, 2003], in which removal of highly soluble species including HBr, HOBr, and BrONO_2 takes place with first-order rates based on the rainfall rate diagnosed within the model convection operator. The model did well in the evaluations for the stratosphere and the upper troposphere and lower stratosphere (UTLS) in CCMVal [Eyring *et al.*, 2010; Gettelman *et al.*, 2010]. The tropospheric chemistry in this model updates the previous version of MOZART2.4 as evaluated and compared with tropospheric observations by Horowitz *et al.* [2003, 2007], but, while the tropospheric values appear to be similar to the earlier evaluations, this model has not undergone the same level of comparisons for the troposphere as was done in the earlier studies.

[18] BTP is expected to react primarily with OH in the atmosphere. This reaction, with the rate constant given in equation (2) above, is the only BTP loss process represented in WACCM for this study. WACCM upper tropospheric temperatures can range below the 220 K minimum temperature of our measurements, but BTP concentrations are minimal in those regions of the atmosphere as will be shown below. Thus, we expect little effect on our model results from temperature extrapolation below the range of equation (2). Other tropospheric reactions besides that with OH are possible for this brominated alkene, including reactions with such oxidants as O_3 , NO_3 , and Cl, but their rate parameters are currently unknown. Photolysis is also a possible loss process, but the absorption cross sections decrease rapidly for wavelengths longer than 220 nm [Orkin *et al.*, 2002] while solar flux at wavelengths shorter than 300 nm at altitudes below stratospheric O_3 is negligible, suggesting that photolysis of BTP is unimportant below the stratospheric O_3 layer. Any BTP reactions in the troposphere in addition to that with OH will reduce its atmospheric lifetime, decreasing its climate and ozone effects compared to our results below.

[19] For this combined ozone and climate effects study, we should consider the possible production of compounds with longer atmospheric lifetimes than BTP, whether or not they contain bromine. While yields of BTP oxidation products under atmospheric conditions have not been measured, we

expect OH to add to either alkene carbon. The most likely initial products of OH addition at the 1-carbon are $\text{Br} + \text{CF}_3\text{C}(\text{O})\text{CH}_2\text{OH}$, and those for OH addition at the 2-carbon are $\text{CH}_2\text{O} + \text{CF}_3\text{CBrO}$. The rate constant for OH reaction with $\text{CF}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ is currently not available, and the following estimation of its tropospheric chemistry is speculative. The OH reaction rate constant with $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ [Atkinson *et al.*, 2006] (citation as updated on the IUPAC Subcommittee on Gas Kinetic Data Evaluation Web site <http://www.iupac-kinetic.ch.cam.ac.uk/>, Data Sheet HO_x_VOC32, 18 December 2007) suggests that $\text{CF}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ could react with OH nearly as quickly as does BTP, yielding CH_2O plus the $\text{CF}_3\text{C}(\text{O})\text{O}_2$ radical. However, OH reaction of $\text{CF}_3\text{C}(\text{O})\text{CH}_3$ is at least 10 times slower than that of OH with $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ (J. A. Manion *et al.*, NIST Chemical Kinetics Database: NIST Standard Reference Database 17, Version 7.0 (Web), Release 1.4.3, Data version 2008.12, Natl. Institute of Standards and Technology, <http://kinetics.nist.gov>). If fluorination slows the OH rate constant of $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ by as large a factor, $\text{CF}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ could have an atmospheric chemical lifetime of several months. Even so, $\text{CF}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ is likely to be soluble on cloud water, so that wet deposition should remove it rapidly from the atmosphere. The product of OH addition at the 2-carbon of BTP, CF_3CBrO , is a possible bromine carrier for which we have found no photochemical reaction data. The acetyl halides CH_3CXO (X = Cl, Br, or I) are known to react readily with liquid water [e.g., Devore and O'Neal, 1969]; by analogy, we expect CF_3CBrO should be water-soluble and will react quickly by hydrolysis on clouds or aerosols to yield $\text{HBr} + \text{CF}_3\text{C}(\text{O})\text{OH}$. CF_3CBrO could also be expected to photolyze to release Br atom and produce $\text{CF}_3\text{C}(\text{O})\text{O}_2$, the same result as from oxidation of the other initial BTP + OH product $\text{CF}_3\text{C}(\text{O})\text{CH}_2\text{OH}$, but the photolysis rate for this additional loss process is unknown. The $\text{CF}_3\text{C}(\text{O})\text{O}_2$ radical is expected to mostly produce CF_3OH in the atmosphere, but one channel of its reaction with HO_2 can produce $\text{CF}_3\text{C}(\text{O})\text{OH}$. In summary, we believe the most important eventual oxidation products to be bromine atom Br plus CH_2O (formaldehyde), $\text{CF}_3\text{C}(\text{O})\text{CH}_2\text{OH}$, CF_3OH , (trifluoromethanol) and CF_3COOH (trifluoroacetic acid, also called TFA), in proportions that depend on the speed of $\text{CF}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ wet deposition versus OH reaction. $\text{CF}_3\text{C}(\text{O})\text{OH}$ is subject to wet deposition, and can react with OH to produce CF_3OH . CF_3OH is relatively unreactive in the troposphere, and thus should primarily be removed by rainout. We include a diagram of our estimated BTP + OH oxidation scheme in the auxiliary material for this article. Our WACCM runs for this study assume immediate availability of the atomic Br reaction product from BTP upon reaction with OH and neglect other possible products, so that this study considers only direct climate effects of BTP.

[20] The ODP of short-lived gases depends on the latitude at which the gases are emitted. For BTP, we choose two emission scenarios similar to those used in the recent study of the candidate replacement compound n-propyl bromide [Wuebbles *et al.*, 2011]. Although one anticipated use of BTP is in airline cabins, handheld fire extinguishers are only used rarely in flight, so that all BTP emissions are assumed to occur at ground level in this study. BTP is emitted at a total rate of 5.0 Tg yr^{-1} in both scenarios, an emission rate which is chosen to give a numerically significant O_3 impact in the atmospheric model for the ODP derivation. Neither

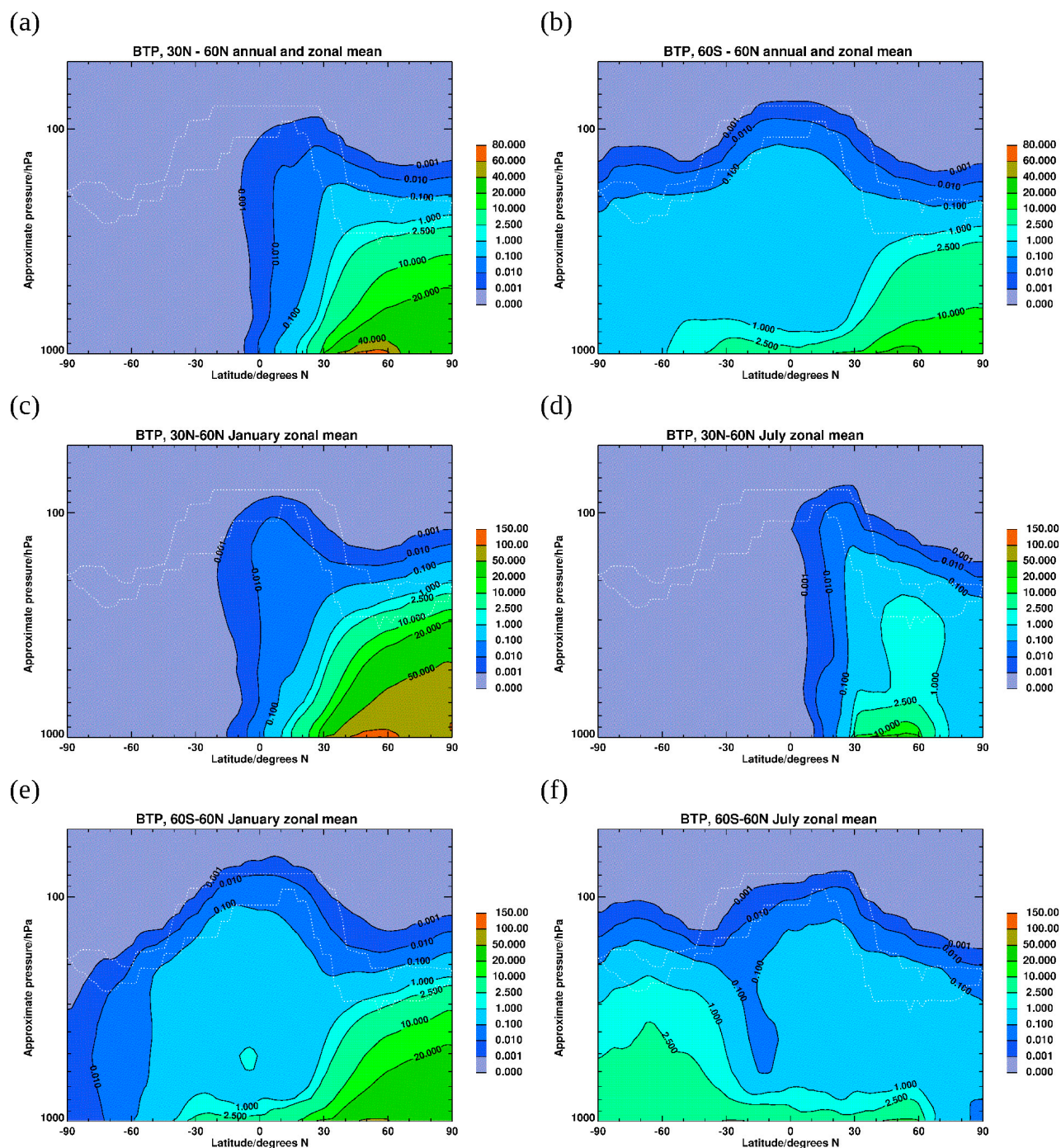


Figure 4. Zonal mean mixing ratios in ppt of 2-bromo-3,3-trifluoropropene (BTP) calculated in the Whole Atmosphere Community Climate Model for 5.0 Tg yr^{-1} total flux from land surfaces. For these and Figures 5–7, white dotted lines identify the minimum and maximum pressure of the tropopause. (a) Annual average, emission from 30°N to 60°N . (b) Annual average, emission from 60°S to 60°N . (c) Emission from 30°N to 60°N , January. (d) Emission from 30°N to 60°N , July. (e) Emission from 60°S to 60°N , January. (f) Emission from 60°S to 60°N , July.

emissions scenario is intended to represent a projection of anticipated use. In each scenario, the BTP emissions are from land surfaces and are constant with time of year. The first scenario emits 1.15×10^9 molecules BTP $\text{cm}^{-2} \text{ s}^{-1}$ uniformly at all landmasses from 30°N to 60°N latitude, a latitude range which includes most of the existing

industrialized nations. The second scenario emits 4.60×10^8 molecules BTP $\text{cm}^{-2} \text{ s}^{-1}$ uniformly at all land surfaces from 60°S to 60°N latitude, which represents an extension of BTP use worldwide in a way consistent with past “global” n-propyl bromide emissions scenarios [Wuebbles *et al.*,

Table 2. Atmospheric Burden in Gigagrams of 2-Bromo-3,3,3-Trifluoropropene (BTP) Due to Emissions of 5.0 Tg yr⁻¹ BTP Into the Whole Atmosphere Community Climate Model (WACCM)^a

Emissions Scenario	Troposphere		Stratosphere and Above	
	Burden (Gg)	Percent of Total	Burden (Gg)	Percent of Total
30°N to 60°N	95.95	99.71	0.28	0.29
60°S to 60°N	58.81	99.67	0.19	0.33

^aThe tropopause is defined according to the WMO thermal tropopause definition, the altitude at which the decrease of temperature falls below 2 K km⁻¹, constrained to a range of 6 to 18 km.

2001]. Each scenario required eight model years to reach near-steady state for ODP calculations.

[21] A separate WACCM scenario used a surface CFC-11 mixing ratio increase of 80 ppt to obtain a percent change in global O₃ burden, -0.372%, and a 0.0304 Tg CFC-11 yr⁻¹ increase in CFC-11 chemical removal rate (equal to surface flux) for the denominator of the ODP calculation. This and the unperturbed WACCM run required nine years of model time to achieve a year-to-year near-steady state adequate for the ODP calculation.

4.2. BTP in the Atmosphere

[22] Because BTP reacts quickly in the troposphere, its mixing ratios are expected to decrease rapidly away from the region of emissions along both latitude and altitude. Figure 4 shows the BTP zonal average mixing ratios in ppt for the two emission scenarios. In these and following figures of latitude as horizontal axis and approximate pressure (based on the hybrid sigma-pressure coordinates used in the model) as vertical, the two dotted white lines indicate thermal tropopause minimum and maximum pressures over all longitudes and months incorporated in each figure. The annually averaged zonal mean BTP mixing ratio for 30°N to 60°N land emissions is shown in Figure 4a, and that for 60°S to 60°N is shown in Figure 4b. The maximum annual and zonal average BTP mixing ratio, 78.4 ppt for 30°N to 60°N and 31.3 ppt for 60°S to 60°N, is at the boundary between 50°N and 60°N in each of the figures. BTP is indeed mostly constrained to the Northern troposphere in the 30°N to 60°N emissions case, such that the highest BTP mixing ratio at the tropopause maximum pressure in Figure 4a is 2.5 ppt, located at 70°N to 80°N. For the 60°S to 60°N emissions case in Figure 4b, the highest BTP mixing ratio at the maximum tropopause pressure is 1.0 ppt located between 55°N and 80°N.

[23] Because BTP has an atmospheric lifetime much shorter than one year toward reaction with OH, and OH concentrations increase with increased solar flux, the mixing ratio of BTP can be expected to exhibit seasonal dependence opposite in phase to that of the local OH concentration. Figures 4c and 4d show the January and July zonal average BTP mixing ratios for the 30°N to 60°N, 5.0 Tg yr⁻¹ scenario. Throughout the atmosphere, the July mixing ratios for BTP (Figure 4d) are smaller than those in January (Figure 4c). Similarly, the 60°S to 60°N, 5.0 Tg yr⁻¹ BTP emissions result in overall larger mixing ratios in January (Figure 4e) than in July (Figure 4f), which is because most land in the range of emissions latitudes is in the Northern Hemisphere.

[24] BTP burdens in Gg and the fraction of BTP are given for the model troposphere and for the stratosphere to top of atmosphere in Table 2 for each of the scenarios. For the 30°N to 60°N scenario, 0.29% of the BTP burden is above the tropopause. For 5.0 Tg yr⁻¹ of BTP emitted from land between 60°S and 60°N, 0.33% of the BTP burden is above the tropopause. The minimal percentage of BTP reaching the stratosphere indicates that most of the BTP is oxidized in the troposphere.

[25] The BTP burden also is the numerator for the atmospheric lifetime calculation; the denominator is the loss rate of BTP due to chemical reaction. Our WACCM runs are set up to include the BTP chemical loss rate in the output, and we have used that information saved from the 5.0 Tg yr⁻¹ scenarios to calculate BTP lifetimes shown in Table 3. The 7.0 day lifetime obtained for the 30°N to 60°N land emissions scenario and the 4.3 day lifetime obtained for the 60°S to 60°N land emissions scenario are among the shortest we have ever found in an ODP or GWP evaluation for a candidate replacement compound. We also separately tested BTP lifetimes in 2.0 Tg yr⁻¹ BTP emission scenarios (not shown in Table 3), and those were higher by less than one percent than the lifetimes obtained from the 5.0 Tg yr⁻¹ emissions scenarios, suggesting that the model response to BTP should scale linearly with flux.

4.3. Atmospheric Bromine From BTP

[26] BTP mixing ratios in the model stratosphere (altitudes above the minimum thermal tropopause pressure) do not exceed 1 ppt in either 5.0 Tg yr⁻¹ emissions scenario, which suggests that no more than this mixing ratio of inorganic bromine (Br_y) can result from direct BTP oxidation in the stratosphere. Figure 5 shows zonal mean Br_y perturbations resulting from the 5.0 Tg yr⁻¹ BTP emissions scenarios. The annual average, zonal mean Br_y perturbation from the 30°N to 60°N land emissions scenario in Figure 5a shows a non-symmetric profile, with Br_y increases in the Southern and tropical troposphere limited to less than 0.1 ppt. The maximum Br_y increase appears as a region starting from the emissions latitudes and reaching to the Northern upper troposphere and lower stratosphere (UTLS). Most of the stratosphere for this scenario has Br_y mixing ratio increases from BTP no greater than 1.0 ppt. The 60°S to 60°N emissions scenario annual and zonal mean in Figure 5b also shows little sign of stratospheric Br_y increases from BTP larger than 1 ppt. Within the troposphere, however, the figure is more symmetric with a second region of Br_y perturbation in the Southern Hemisphere.

[27] Figure 5 suggests that there will be only a tiny fraction of Br_y reaching the stratosphere either directly or indirectly from BTP oxidation. Table 4 lists the Br_y burden changes in Gg Br arising from BTP in the model troposphere

Table 3. Atmospheric Lifetimes and Ozone Depletion Potentials (ODPs) of 2-Bromo-3,3,3-Trifluoropropene for 5.0 Tg yr⁻¹ Emissions From Land Surfaces in WACCM

Emissions Scenario	Atmospheric Lifetime (days)	ODP
30°N to 60°N	7.0	0.0028
60°S to 60°N	4.3	0.0052

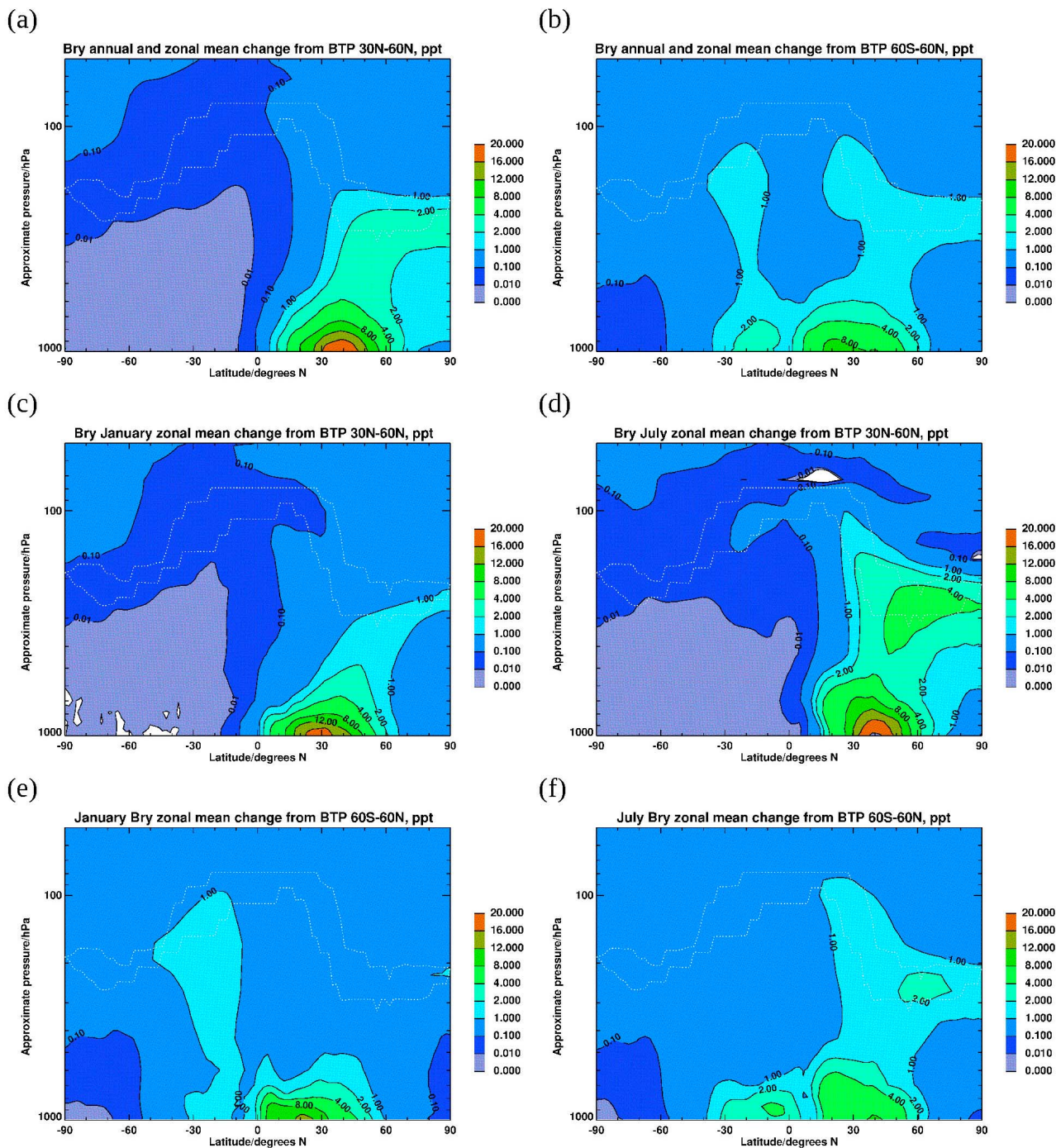


Figure 5. Zonal mean changes in mixing ratio (ppt) of inorganic bromine species (Br_y) resulting from 5.0 Tg yr^{-1} flux of BTP from land surfaces. (a) Annual average, emission from 30°N to 60°N . (b) Annual average, emission from 60°S to 60°N . (c) Emission from 30°N to 60°N , January. (d) Emission from 30°N to 60°N , July. (e) Emission from 60°S to 60°N , January. (f) Emission from 60°S to 60°N , July.

and above the thermal tropopause for the two emissions scenarios. For the 30°N to 60°N , 5.0 ppt scenario, only 3.1% of the Br_y perturbation is above the tropopause; for the 60°S to 60°N , 5.0 ppt scenario, 7.8% of the Br_y perturbation is above the tropopause, largely because of the strong transport in the Hadley circulation in the tropics.

[28] The pattern in the annual average, zonal mean Br_y perturbations of Figures 5a and 5b could be interpreted to

Table 4. Derived Burden Perturbation of Inorganic Bromine Species (Br_y) in Gigagrams Br Due to 5.0 Tg yr^{-1} Surface Emissions of 2-Bromo-3,3,3-Trifluoropropene in WACCM

Emissions Scenario	Troposphere	Stratosphere and Above	Stratosphere Percent of Total
30°N – 60°N	17.93	0.58	3.1
60°S – 60°N	18.68	1.58	7.8

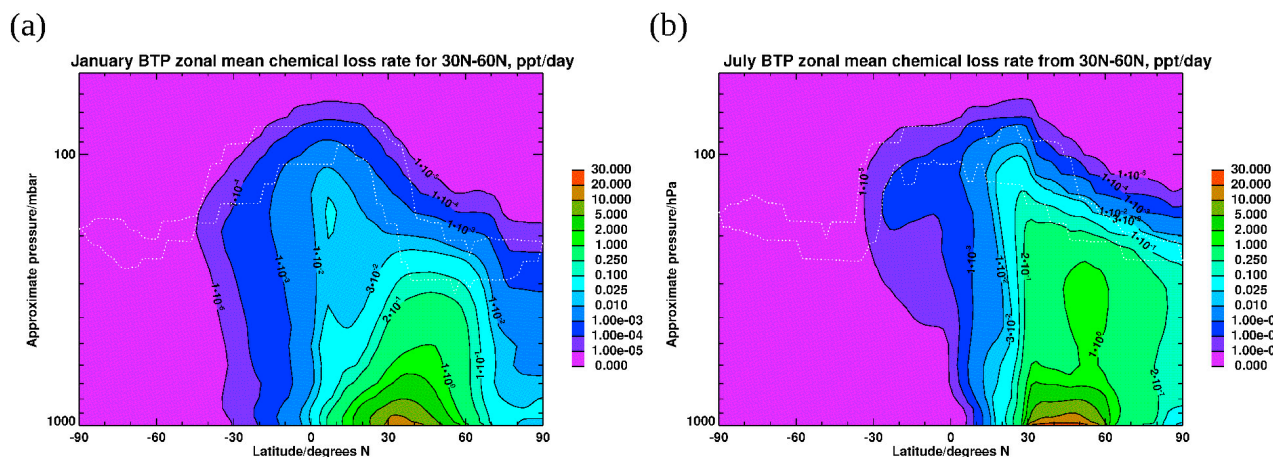


Figure 6. Zonal, monthly mean 2-bromo-3,3,3-trifluoropropene (BTP) chemical loss rates (ppt day^{-1}) for 5.0 Tg yr^{-1} flux of BTP from land surfaces at latitudes 30°N to 60°N . (a) January. (b) July.

indicate that BTP lifted to the UTLS is oxidized there. The January Br_y perturbation for the 30°N to 60°N , 5.0 Tg yr^{-1} land emissions scenario is shown in Figure 5c, and that for July in Figure 5d. July Br_y perturbations in the Northern UTLS peak above 5 ppt, markedly larger than the 1 ppt maximum for that region in January, though no more than 1 ppt BTP reaches the UTLS in July (Figure 4d). The January (Figure 5e) and July (Figure 5f) Br_y perturbation plots for the 60°S to 60°N scenario show that the BTP reaches the UTLS in whichever hemisphere is in summer. While these figures do not definitely distinguish transport as BTP followed by oxidation to Br_y from BTP oxidation to Br_y near the boundary layer followed by transport upward, they indicate that WACCM convection is involved in sending Br_y from BTP to the stratosphere. The zonal-mean chemical loss rate of BTP in ppt day^{-1} for the 30°N to 60°N , 5.0 Tg yr^{-1} land emissions scenario is shown in Figure 6a for January and in Figure 6b for July. In both months, BTP removal rates of tens of ppt day^{-1} occur near the emissions region, and the removal rate decreases with altitude. However, the July BTP removal rate (Figure 6b) decreases less strongly with increased altitude than does that in January (Figure 6a), suggesting contributions from convection of BTP and of Br_y produced from BTP near the surface to the Br_y perturbation reaching the UTLS.

4.4. Ozone Effects of BTP

[29] Because of the limited fraction of Br_y reaching the stratosphere, much of the BTP effect on O_3 is derived to occur in the troposphere as shown below. The global and annual mean percentage change of O_3 in the model due to 5.0 Tg yr^{-1} BTP is shown in Figure 7. In both the 30°N to 60°N (Figure 7a) and 60°S to 60°N (Figure 7b) scenarios, the largest percentage decreases are in the troposphere. The 30°N to 60°N land emissions scenario in Figure 7a shows small O_3 loss percentages in the stratosphere, with the peak values of about -0.5% near the tropopause outside the tropics. The greater fraction of stratospheric Br_y (Table 4) for the 60°S to 60°N scenario leads to O_3 losses in Figure 7b of up to 1.0% in the Northern lower stratosphere and nearly 2% in the Southern lower stratosphere. Seasonal dependence of O_3 percentage loss due to BTP (Figures 7c and 7d for January and July, 30°N to 60°N ; Figures 7e and 7f for

January and July, 60°S to 60°N) is limited in the stratosphere, maximized in the summer troposphere for either hemisphere, and minimal in the Southern troposphere for the 30°N to 60°N scenario.

[30] Though O_3 percent losses are largest in the troposphere, those are relative to the small O_3 mixing ratios there compared to the stratosphere. The integrated total column of O_3 from top of atmosphere determines the extent to which harmful ultraviolet is prevented from reaching the surface, and is therefore the criterion for determining ODP. Changes in Tg of O_3 burden for the WACCM troposphere and for the stratosphere and above resulting from 5.0 Tg yr^{-1} of BTP land emissions are listed in Table 5. Despite the low fractions of Br_y perturbation reaching the stratosphere given in Table 4, the O_3 burden loss above the tropopause is 27% for the 30°N to 60°N scenario and 46% , or nearly half, for the 60°S to 60°N scenario.

[31] The ODP is obtained through the equation

$$\text{ODP}(X) = \frac{\Delta \text{O}_3 \text{ burden}(X)}{\Delta \text{O}_3 \text{ burden}(\text{CFC} - 11)} \frac{\text{CFC} - 11 \text{ flux}}{X \text{ flux}} \quad (3)$$

The change in total O_3 burden due to 80 ppt surface mixing ratio increase of CFC-11 in WACCM, relative to the reference atmosphere burden of 3139.0 Tg , was given above as -0.372% , and the corresponding CFC-11 flux increase is $0.0304 \text{ Tg yr}^{-1}$. 5.0 Tg yr^{-1} of BTP is applied directly in equation (3), and the percent change in total O_3 burden due to BTP is -0.170% for 30°N to 60°N , 5.0 Tg yr^{-1} and -0.315% for 60°S to 60°N , 5.0 Tg yr^{-1} . These values provide the ODPs in Table 3. The 30°N to 60°N BTP ODP of 0.0028 is the smallest we have obtained for a brominated species thus far. Even the 60°S to 60°N ODP of 0.0052 is a factor of nearly 20 times less than the 0.1 limit called for in the U.S. Clean Air Act. A full error analysis of WACCM is not practical at this time. The potential bromine-containing BTP oxidation product CF_3CBrO noted in Section 4.1 is likely a major part of the uncertainty in the ODP. However, most BTP oxidation to products including CF_3CBrO occurs in the lower to middle troposphere, where clouds are often present and highly soluble species will be removed rapidly in rainout. CF_3CBrO is likely to dissolve readily and rapidly

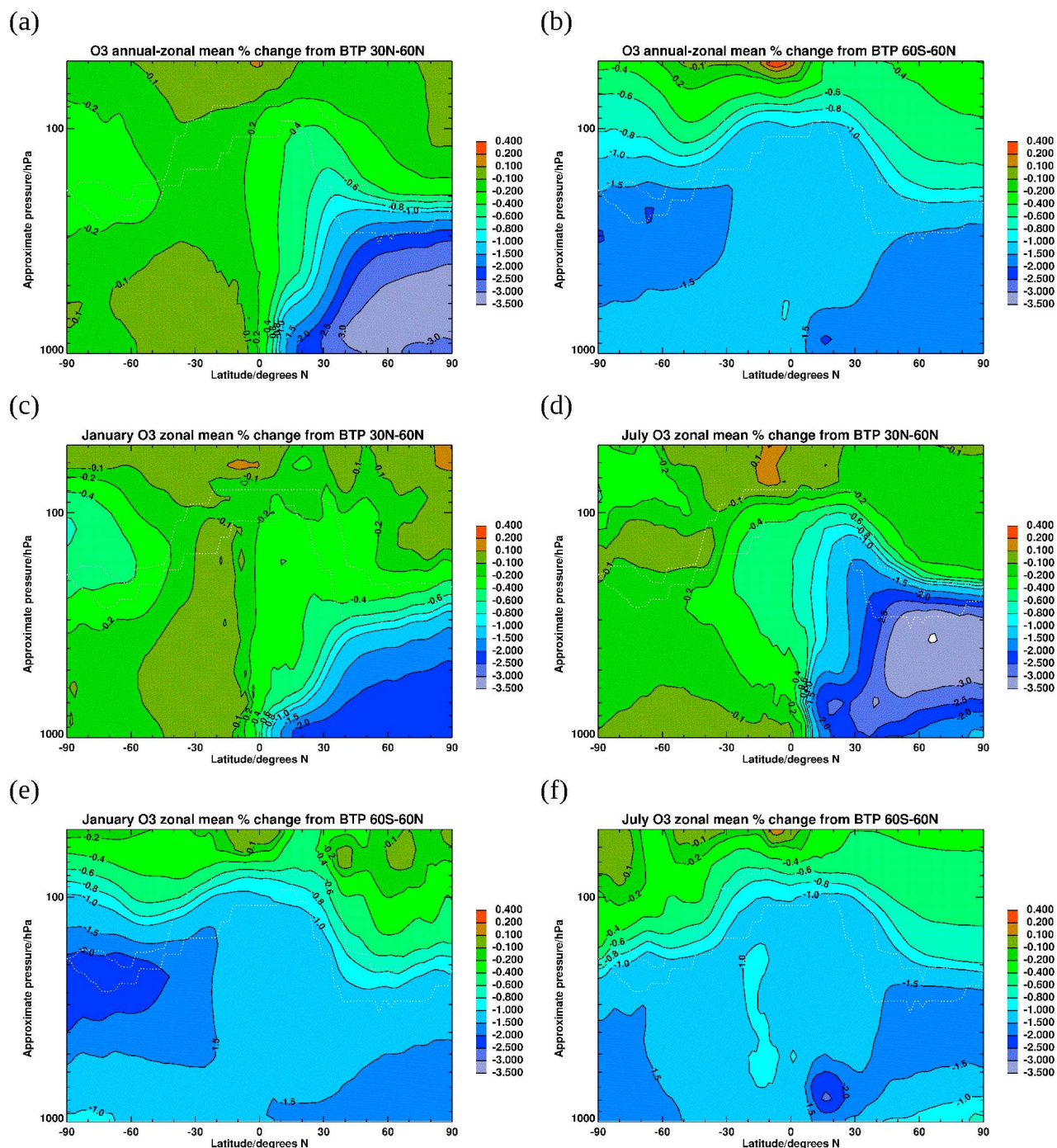


Figure 7. Zonal mean percent changes in mixing ratio of ozone (O_3) resulting from 5.0 Tg yr^{-1} flux of BTP from land surfaces. (a) Annual average, emission from 30°N to 60°N . (b) Annual average, emission from 60°S to 60°N . (c) Emission from 30°N to 60°N , January. (d) Emission from 30°N to 60°N , July. (e) Emission from 60°S to 60°N , January. (f) Emission from 60°S to 60°N , July.

hydrolyze on cloud water, which could lower the actual BTP ODP somewhat compared to this study. However, even if CF_3CBrO were as long-lived as BTP in the troposphere, it would increase BTP O_3 loss and ODP by up to a factor of two compared to our model results. Such an increase in ODP compared to the current study would still indicate minimal O_3 loss from BTP.

Table 5. Derived Changes in Ozone (O_3) Burdens in Teragrams Due to 5.0 Tg yr^{-1} Surface Emissions of 2-Bromo-3,3,3-Trifluoropropene in WACCM

Emissions Scenario	Troposphere	Stratosphere and Above	Stratosphere Percent of Total
30°N – 60°N	−3.92	−1.43	27
60°S – 60°N	−5.39	−4.51	46

[32] Brioude *et al.* [2010] recently studied the variation of ODP with emission region and season for several short-lived gases, including BTP, in a Lagrangian model driven by mid-2000s meteorological data from the European Centre for Medium-Range Weather Forecasts. The general conclusions of Brioude *et al.* [2010], including its auxiliary material, were that ODP increases with decreased emissions latitude and with summer compared to winter. Our higher ODPs for land emissions from 60°S to 60°N than from 30°N to 60°N are consistent with the Brioude *et al.* latitude dependence, and our higher values of UTLS BTP, Br_y perturbation and % change of O₃ in the 30°N to 60°N scenario for July (Figures 4d, 5d, and 7d, compared to Figures 4c, 5c, and 7c for January) are consistent with the summer ODP increase reported by Brioude *et al.* While the emission regions used by Brioude *et al.* [2010] are not identical to those in this study, their annual average ODP reported for midlatitude North America, 0.0035, is slightly higher than our 30°N to 60°N value of 0.0028. The annually averaged, global BTP lifetime of 4.4 days reported for the midlatitude North America emission region in Brioude *et al.* is shorter than our 7.0 day lifetime for the 30°N to 60°N land emissions scenario and more consistent with 4.3 days which we found for the 60°S to 60°N scenario (Table 3), though the Brioude *et al.* emission region seems to range from about 23°N to 55°N. Differences between Brioude *et al.* and our study may arise from differences in BTP emissions distributions or from dynamic parameterizations in our model versus those from Brioude *et al.*, but may also result from the details of BTP chemical loss processes in the two models: our model evaluates OH loss of BTP within its chemical solver with an external time step of 30 min, while the Brioude *et al.* [2010] study calculates BTP loss from daily averaged OH concentrations derived from MOZART 4.

4.5. Climate Effects of BTP

[33] We apply the University of Illinois at Urbana-Champaign radiative transfer model (UIUC RTM) to obtain GWPs from the WACCM outputs. The UIUC RTM calculates fluxes of solar and of terrestrial radiation across the tropopause for input atmospheres supplied by models. Earlier versions of the UIUC RTM have been applied to several studies of climate effects and GWPs [Jain *et al.*, 2000; Naik *et al.*, 2000; Youn *et al.*, 2009]. The UIUC RTM was originally based on the radiative transfer models of the Community Climate Model (CCM) [Briegleb, 1992a, 1992b]. The solar model includes 18 spectral bins from 0.2 to 5.0 microns and incorporates absorption by H₂O, O₃, O₂, CO₂, clouds, and the surface along with scattering processes by clouds, gas-phase molecules, and the surface. Terrestrial radiation is calculated with a narrow band model of absorptivity and emissivity over the wave number range 0 to 3000 cm⁻¹ at resolutions of 5 cm⁻¹ for CO₂, O₃, CH₄, and N₂O and of 10 cm⁻¹ for H₂O, CFC-11, and CFC-12. The infrared absorption parameters for these gases are based on the HITRAN 2004 database [Rothman *et al.*, 2005]. The BTP infrared cross sections measured in this study are regridded to 10 cm⁻¹ resolution for the UIUC RTM. Observation-based surface albedo and surface emissivity are used with clouds based on the International Satellite Cloud Climatology Project.

[34] To obtain GWP for BTP, we must obtain the change in net downward radiative flux across the tropopause, or tropopause radiative forcing (RF), due to the BTP distribution we have calculated in our model. We apply the UIUC RTM with the BTP infrared cross sections measured above as shown in Figure 3 to our WACCM outputs. The RTM obtains tropopause RF for the reference run (without BTP) and for the two BTP emissions scenarios, and the difference in tropopause RF is used in the further calculations. The tropopause RF change due to BTP in the 30°N to 60°N land emissions scenario is 0.000112 W m⁻², and that for the 60°S to 60°N land emissions scenario is 0.000102 W m⁻². It must be noted that these are instantaneous RF perturbations; the magnitudes of these perturbations, when compared to net terrestrial radiation fluxes across the tropopause that average some 220 W m⁻², are small enough that stratospheric temperature adjustment is unlikely to be significant for BTP.

[35] The GWP is calculated as the ratio of tropopause RF integrated over time to a time horizon t_H (also known as absolute GWP or AGWP) resulting from a pulse release compound to that from a pulse release of the same mass of CO₂. We assume that BTP would be removed with a single-exponential decay at its atmospheric lifetime τ if its emissions stopped, so that the AGWP for BTP is given by

$$AGWP = F_0 \tau \left[1 - \exp\left(-\frac{t_H}{\tau}\right) \right] \quad (4)$$

where the radiative forcing per kg of BTP F_0 is obtained by dividing the tropopause RF perturbation by the annual flux of 5.0 Tg yr⁻¹, or 5.0×10^9 kg yr⁻¹. t_H frequently is specified as 20, 100, or 500 years for long-lived gases. The lifetime of BTP in the 30°N to 60°N emissions scenario is 7.0 days and that in the 60°S to 60°N emissions scenario is 4.3 days (Table 3), so that the exponential term in equation (4) is effectively zero for even $t_H = 20$ years. Thus, the AGWPs for BTP at 20, 100, or 500 years are equal to radiative forcing per kg BTP times lifetime:

$$30^\circ\text{N} - 60^\circ\text{N AGWP} = 4.3 \times 10^{-16} \text{ W m}^{-2} \text{ yr (kg BTP)}^{-1}$$

$$60^\circ\text{S} - 60^\circ\text{N AGWP} = 2.4 \times 10^{-16} \text{ W m}^{-2} \text{ yr (kg BTP)}^{-1}.$$

[36] The IPCC 2006 report [Forster *et al.*, 2007] Section 2.10.2 supplies AGWPs for CO₂ at $t_H = 20, 100$, and 500 years:

$$20 \text{ year AGWP} = 2.47 \times 10^{-14} \text{ W m}^{-2} \text{ yr (kg CO}_2\text{)}^{-1}$$

$$100 \text{ year AGWP} = 8.69 \times 10^{-14} \text{ W m}^{-2} \text{ yr (kg CO}_2\text{)}^{-1}$$

$$500 \text{ year AGWP} = 28.6 \times 10^{-14} \text{ W m}^{-2} \text{ yr (kg CO}_2\text{)}^{-1}$$

Dividing these into the BTP AGWP provides the GWP values shown on the upper lines in Table 6. These low GWPs suggest that the climate effect of BTP will be markedly smaller than that of an equivalent mass of CO₂ from, for example, fossil fuel combustion.

[37] We are unaware of other reports of GWP for BTP, but the GWPs reported in this study are considerably lower than

Table 6. Global Warming Potentials (GWPs) for 2-Bromo-3,3,3-Trifluoropropene (BTP) for Time Horizons t_H of 20, 100, and 500 Years Derived From WACCM and the UIUC RTM^a

Emissions Scenario	$t_H = 20$ yr	$t_H = 100$ yr	$t_H = 500$ yr
30°N to 60°N	0.017	0.0050	0.0015
60°S to 60°N	0.0097	0.0028	0.00084
Well-mixed estimate	2.1	0.59	0.18

^aBTP GWPs based on a tropospherically well-mixed approximation are also shown for comparison.

GWPs reported for many other short-lived halocarbons. Such GWPs are usually based on a well-mixed approximation in which the halocarbon is assumed to be thoroughly mixed in the troposphere. However, this approximation is not realistic for compounds with atmospheric lifetimes markedly shorter than one year such as BTP. Figure 4 illustrates that BTP mixing ratios derived in WACCM do not satisfy the well-mixed approximation. BTP mixing ratios in the upper troposphere and lower stratosphere where most of its radiative forcing effect is expected are markedly lower than near the surface emissions region. We show well-mixed approximation GWPs for BTP in Table 6 for comparison to our model-derived GWPs. The well-mixed BTP GWPs are based on a radiative efficiency of $0.193 \text{ W m}^{-2} \text{ ppb}^{-1}$ obtained from the IR cross sections in this report by the method of Pinnock *et al.* [1995] and a well-mixed approximation atmospheric lifetime of 3.0 days estimated by scaling the OH lifetime of methyl chloroform [Prinn *et al.*, 2001; Spivakovsky *et al.*, 2000] by the ratio of OH rate constants at an average tropospheric temperature of 270 K. These well-mixed approximation GWPs are over 100 times larger than our model-derived GWPs. Many GWPs previously reported for short-lived compounds are upper limits based on the well-mixed approximation, and it should be emphasized that model-based profiles for very short-lived compounds could result in markedly smaller GWPs than have been previously reported.

5. Conclusions

[38] The OH reaction rate constant for temperatures from 220 to 370 K and the IR absorption cross sections of 2-bromo-3,3,3-trifluoropropene (BTP) were measured in this study. The measured OH reaction rate constant can be represented as $k_{\text{BTP}}(T) = 4.85 \times 10^{-13} \times (T/298)^{0.92} \times \exp(+613/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ over the entire T range of measurements. For atmospheric modeling, we recommend the Arrhenius expression $k_{\text{BTP}}(T) = 1.05 \times 10^{-12} \times \exp(+381/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. We have also evaluated the potential effects of BTP on ozone and climate in the form of ODPs and GWPs for assumed land-based emissions at latitudes 30°N to 60°N and at latitudes 60°S to 60°N with a rate of 5.0 Tg yr^{-1} (selected to provide an ozone burden decrease of at least 0.1%, not as a reflection of anticipated BTP use) with the Whole Atmosphere Community Climate Model. BTP is among the shortest-lived of bromocarbons evaluated thus far, with a lifetime of 7.0 days for 30°N to 60°N emissions and of 4.3 days for 60°S to 60°N emissions. The Ozone Depletion Potential (ODP) obtained for the 30°N to 60°N emissions scenario is 0.0028, one of the lowest of any candidate

replacement compound we have studied, and that and the 0.0052 ODP for 60°S to 60°N emissions indicate that BTP would have an insignificant effect on ozone. The direct Global Warming Potential (GWP) of BTP at a 100-year time horizon is estimated to be 0.0050 for the 30°N to 60°N emissions scenario and 0.0028 for the 60°S to 60°N emissions scenario. These small ODP and GWP values suggest that the environmental effects of BTP will be minimal for any reasonable level of emission expected for this candidate fire-extinguishing replacement compound.

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