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New methodology for Ozone Depletion Potentials of short-lived compounds: n-Propyl bromide as an example

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Abstract. A number of the compounds proposed as replacements for substances controlled under the Montreal Protocol have extremely short atmospheric lifetimes, on the order of days to a few months. An important example is n-propyl bromide (also referred to as 1-bromopropane, $CH_2BrCH_2CH_3$ or simplified as 1-C_3H_7Br or nPB). This compound, useful as a solvent, has an atmospheric lifetime of less than 20 days due to its reaction with hydroxyl. Because nPB contains bromine, any amount reaching the stratosphere has the potential to affect concentrations of stratospheric ozone. The definition of Ozone Depletion Potentials (ODP) needs to be modified for such short-lived compounds to account for the location and timing of emissions. It is not adequate to treat these chemicals as if they were uniformly emitted at all latitudes and longitudes as normally done for longer-lived gases. Thus, for short-lived compounds, policymakers will need a table of ODP values instead of the single value generally provided in past studies. This study uses the MOZART2 three-dimensional chemical-transport model in combination with studies with our less computationally expensive two-dimensional model to examine potential effects of nPB on stratospheric ozone. Multiple facets of this study examine key questions regarding the amount of bromine reaching the stratosphere following emission of nPB. Our most significant findings from this study for the purposes of short-lived replacement compound ozone effects are summarized as follows. The degradation of nPB produces a significant quantity of bromoacetone which increases the amount of bromine transported to the stratosphere due to nPB. However, much of that effect is not due to bromoacetone itself, but instead to inorganic bromine which is produced from tropospheric oxidation of nPB, bromoacetone, and other degradation products and is transported above the dry and wet deposition processes of the model. The MOZART2 nPB results indicate a minimal correction of the two-dimensional results in order to derive our final results: an nPB chemical lifetime of 19 days and an Ozone Depletion Potential range of 0.033 to 0.040 for assumed global emissions over landmasses, 19 days and 0.021 to 0.028, respectively, for assumed emissions in the industrialized regions of the Northern Hemisphere, and 9 days and 0.087 to 0.105, respectively, for assumed emission in tropical Southeast Asia.

1. Introduction

Emissions of halogenated gases containing chlorine, bromine, or iodine have the potential to affect stratospheric ozone concentrations if sufficient amounts of these compounds or their degradation products reach the stratosphere. The use of such chemicals is generally evaluated by policymakers through consideration of the Ozone Depletion Potential (ODP) for each compound, following the Montreal Protocol and the U.S. Clean Air Act [*Wuebbles*, 1981, 1983; *World Meteorological Organization* (*WMO*), 1992, 1995, 1999]. Traditionally, ODPs have been primarily evaluated through the use of zonally averaged, two-dimensional chemical-transport models of the global atmosphere. These models have been the primary tools used in studies of stratospheric processes because most chemicals evaluated for ODPs have had atmospheric lifetimes sufficiently long that they would be well mixed in the troposphere.

However, a number of the compounds recently being proposed as replacements for substances controlled under the Montreal Protocol have extremely short atmospheric lifetimes, on the order of days to a few months. An important example is n-propyl bromide (also referred to as 1-bromopropane, $CH_2BrCH_2CH_3$ or simplified as 1-C_3H_7Br or nPB). This compound, useful as a solvent, has been estimated to have an atmospheric lifetime of about 11 to 14 days due to its reaction with hydroxyl, OH [*Nelson et al.*, 1997; *Wuebbles et al.*, 1998, 1999a]. As discussed later, we get a somewhat longer lifetime in the present study, largely because of the way the calculation is done relative to the prior analyses. Because nPB contains bromine, any amount reaching the stratosphere has the potential to affect concentrations of stratospheric ozone.

After emission, generally over continents at midlatitudes in the Northern Hemisphere, short-lived chemicals like nPB are not expected to have well mixed concentrations in the troposphere. Winds and other mixing processes in the atmosphere would gradually transport these gases to the tropics where they can most effectively be transported to the lower stratosphere. At the same time, because of the short lifetime, reaction with OH and other chemical loss processes would convert a signif-

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icant fraction of the chemical emitted to its degradation products. The processes affecting resulting degradation products could be quite important as they could act as vehicles for transporting chlorine or bromine to the lower stratosphere. The inorganic bromine compounds produced from tropospheric nPB degradation, if not sufficiently removed by wet deposition, could contribute further to stratospheric bromine, as indicated by *Ko et al.* [1997]. The question of how much of the halogen that would be available to affect stratospheric ozone therefore depends greatly on the complex effects of transport and chemical processes in the troposphere.

Two-dimensional models, because of their zonally averaged nature, are not designed to adequately account for the variations in concentration and transport of such short-lived compounds and their degradation products. As a result, there are questions about the adequacy of the ODPs determined with these models for such chemicals. These questions are further exacerbated by continual reduction in levels of acceptable ODPs for replacement compounds in policy considerations. The relatively small ODPs for such short-lived compounds would still imply relatively small effects on ozone compared to CFCs and other controlled compounds. However, an acceptable level of ozone depletion has not been established.

Evaluations of ODPs for short-lived compounds with three-dimensional chemical-transport models of the troposphere and stratosphere are needed to resolve these questions. In theory, these models should be able to effectively determine the amount of a short-lived chemical and its degradation products reaching the stratosphere and the resulting potential effects on ozone. However, these models are still under development and generally are not ready for such analyses. At this point, most three-dimensional chemical-transport models, including the one used here, have been primarily designed for studies of tropospheric processes and do not have complete representations of the stratosphere and its processes. These models are also computationally intensive, limiting the number of studies that they can be used for with current computing systems. The few models that do have more complete stratospheres are even more computationally intensive.

The definition of ODPs for short-lived compounds also has to be modified to account for locations of emissions, and perhaps for timing of the emissions. It is not adequate to treat these chemicals as if they were uniformly emitted at all latitudes and longitudes as normally done for longer-lived gases. A workshop on short-lived compounds in March 1999 sponsored by the Environmental Protection Agency (EPA) and NASA [*Wuebbles and Ko*, 1999] concluded that ODPs for short-lived compounds should be defined as a function of location (latitude, longitude) and perhaps time of emission. Thus, for short-lived compounds, the single ODP generally provided to policymakers will need to be replaced with a table of ODP values.

This study uses the MOZART2 three-dimensional model in combination with studies with our less computationally expensive two-dimensional model to examine potential effects of nPB on stratospheric ozone. Multiple facets of this study examine key questions regarding the amount of bromine reaching the stratosphere following emission of nPB. First, we examine the question of whether tropospheric oxidation of nPB could produce intermediate products that survive long enough to transfer bromine into the stratosphere. Second, we evaluate whether inorganic bromine produced from nPB oxidation in the troposphere could reach the stratosphere in meaningful quantities and thus affect stratospheric ozone. Finally, we provide estimates of the ODPs for nPB as a function of where the emissions occur. Because of limited computer time, we have used the three-dimensional model only to examine a few cases for the dependence on location of emission.

2. Model Descriptions

2.1. UIUC Two-Dimensional Chemical-Transport Model

The University of Illinois at Urbana-Champaign (UIUC) two-dimensional chemical-radiative-transport model of the global atmosphere attempts to explicitly represent relevant atmospheric physical and chemical processes affecting the composition of the troposphere, stratosphere, and mesosphere [e.g., *Kotamarthi et al.*, 1999; *Naik et al.*, 1999; *Patten et al.*, 1994; *Rahmes et al.*, 1998; *Wuebbles et al.*, 1991, 1997, 1998, 1999a, 1999b]. The current version of the zonally averaged model determines the atmospheric distributions of 66 chemically active atmospheric trace constituents. The model domain extends from pole to pole at a resolution of 5°, and from the ground to 84 km in log-pressure altitude at a resolution of 1.5 km. The model incorporates the important species and relevant chemistry to evaluate the spatially and temporally varying concentrations in the distributions of the O_x, HO_x, NO_y, Cl_y, Br_y, and CH_xO_y constituents affecting the global atmosphere. There are 148 thermal reactions and 52 photolysis reactions in the chemical mechanism, including heterogeneous reactions on stratospheric sulfate aerosols and polar stratospheric clouds (PSCs). Most thermal reaction rate constants are taken from the NASA panel recommendations [*DeMore et al.*, 1997], with updates made as newer data are analyzed.

The transport of chemical species is accomplished through advection, turbulent eddy transport, and convection. Transport of species in the model is self-consistently calculated using the predicted model ozone (and other radiatively important species) and seasonally varying climatological temperatures (based on National Centers for Environmental Prediction (NCEP) analyses). Model transport fields are evaluated by combining the zonal mean momentum equation and the thermodynamic equation into a form that, along with the thermal wind equation, yields a second-order Poisson diagnostic equation for the residual mean meridional stream function. The right-hand side of the stream function equation includes the net heating rate term and all wave forcings. The net heating rate is calculated knowing the temperature and chemical species distributions and includes latent heating. Planetary waves for wave numbers 1 and 2 are included based on the parameterization of *Li et al.* [1995]. Stratospheric values of K_{yy} are calculated using the planetary wave dissipation rate and vorticity for both wave number 1 and 2. Values of K_{zz} due to gravity waves are evaluated. Larger diffusion coefficients are assigned to the troposphere to mimic fast tropospheric mixing. This version of the model uses a seasonally varying tropospheric K_{yy} in order to better represent radon transport to the stratosphere [*Johnson*, 2000]. Convective transport in the model is based on the climatology of *Langner et al.* [1990]. Wet deposition is incorporated for water-soluble species including the inorganic bromine species BrO, HBr, HOBr, and $BrONO_2$ based on the rainout rate of nitric acid. The latest version of the model also has revised surface emissions (e.g., surface NO_x emissions) to make them more consistent with those used in MOZART2 and uses a tropospheric H_2O climatology consistent with those of MOZART2. This version of the model now

gives a partial tropospheric lifetime for methyl chloroform's reaction with OH (total burden of methyl chloroform divided by the tropospheric reaction rate of CH_3CCl_3 + OH) of 5.62 years, consistent with the recommended 5.7 years based on measurements [*Wuebbles et al.*, 1999b; *Madronich et al.*, 1999].

2.2. MOZART2 Three-Dimensional Chemical-Transport Model

We are collaborating with the National Center for Atmospheric Research (NCAR) in development of the MOZART three-dimensional, chemical-transport model of the global atmosphere. MOZART2, the newest available version of the model (L. Horowitz et al., manuscript in preparation, 2001; the previous version, MOZART1, is described by *Brasseur et al.* [1998]) has 2.8° × 2.8° horizontal resolution, and includes 34 vertical levels extending from the surface to 4 hPa (roughly 38 km). Vertical resolution decreases from ~20 m in the boundary layer to ~1.6 km near the upper boundary with enhanced resolution in the vicinity of the tropopause. Currently, MOZART2 calculates the mixing ratios of 56 species taking into account advection, convection, diffusion, surface and in situ emissions, photochemistry, deposition (wet and dry), and includes a detailed parameterization of vertical exchanges in the boundary layer. Dynamical and chemical updates are calculated using a 20 min time step. Meteorological parameters such as temperature, surface pressure, convective mass fluxes, cloud fraction, horizontal wind fields, etc., used to drive MOZART2, are provided from version 3 of the NCAR Community Climate Model (CCM3). The meteorological data are read every 3 hours and linearly interpolated with each time step. Advective process are accomplished using the multidimensional flux form semi-Lagrangian transport scheme of *Lin and Rood* [1996] with a mass fixer applied after each time step as the semi-Lagrangian scheme is not mass conserving. The chemistry system for a standard MOZART2 run includes 120 gas phase reactions, 29 photolytic reactions, and 5 heterogeneous reactions and is typically solved using the fully implicit Euler backward scheme with Newton-Raphson iteration. For the purposes of this study, we have implemented a limited chemistry incorporating OH reactions and photolysis of nPB and bromoacetone (BrAc), based on our two-dimensional degradation chemistry results (see below), for MOZART2 in order to conserve computer time. The OH fields from a standard chemistry simulation with MOZART2 are used in this study, but are scaled to match a partial atmospheric lifetime due to reaction with OH for methyl chloroform of 5.7 years [*Wuebbles et al.*, 1999b].

3. Degradation Chemistry for nPB

The earlier published studies of nPB neglected its degradation chemistry. In this study, we evaluate this chemistry, and, after having demonstrated the potential importance of the degradation products, include the effects of this degradation in our modeling studies. The two-dimensional modeling studies include the corresponding reactions and estimated reaction rates to fully account for the nPB degradation. Because of computational limitations, the degradation chemistry used in the three-dimensional modeling studies was limited to the most important gases, namely, the production of brominated acetone and the production of inorganic bromine.

3.1. Initial Oxidation of nPB

The chemistry and possible outcomes of hydroxyl (OH) abstraction of hydrogen atoms (H) from the first (brominated), second, and third carbon atoms of nPB are summarized in Figures 1a, 1b, and 1c, respectively. These abstractions result in different isomers of the bromoalkyldioxy radicals $C_3H_6BrO_2$, and the different structures of these determine the products of oxidation. Notably, abstraction of H from the first carbon followed by reaction of the resulting 1-$C_3H_6BrO_2$ with itself or NO produces bromine radical (Br) in one oxidation step, and reaction of 1-$C_3H_6BrO_2$ with HO_2 followed by $CH_3CH_2CHBrOOH$ photolysis produces Br in an OH reaction step plus a photolysis step. Although the reaction rate of nPB with OH has recently been studied [*Nelson et al.*, 1997], the distribution of abstraction rates with respect to carbon atom has not yet been evaluated by experiment. As illustrated in the figure, haloalkyldioxy radicals such as those generated by OH oxidation of nPB react rapidly with other species in air including NO, NO_2, HO_2, and themselves, producing the relatively stable nPB degradation products. We calculate site-specific nPB + OH rate constants by normalizing the site-specific, temperature-dependent rate constants predicted by the structure-activity relationship of *Kwok and Atkinson* [1995] to the total nPB + OH temperature-dependent rate constants of *Nelson et al.* [1997]. Photolysis of nPB is estimated as that of methyl bromide and to yield atomic bromine (Br) plus propyl radical.

Figures 1a, 1b, and 1c illustrate the possible outcomes of OH oxidation. Photolysis of nPB in the troposphere contributes only 0.01% of the total tropospheric degradation rate of nPB and can be neglected compared to the OH reaction channels. On the global flux degradation study with "α-based" rainout in Table 2, and on average over the troposphere, H abstraction from nPB by OH occurs at the first carbon 19.7% of the time, at the second carbon 71.2% of the time, and at the third carbon 9.1% of the time. In the degradation chemistry scheme, as shown in Figures 1b and 1c, the reactions of the 2-$C_3H_6BrO_2$ and 3-$C_3H_6BrO_2$ produced by H abstraction from the second and third carbons with itself, NO, HO_2, or NO_2 exclusively produce BrAc ($CH_3C(O)CH_2Br$) and 3-bromopropionaldehyde ($CHOCH_2CH_2Br$), respectively. However, the reactions of 1-$C_3H_6BrO_2$ produced by H abstraction from the first nPB carbon with NO or itself produce a radical that promptly ejects Br, as illustrated in Figure 1a. The NO reaction causes Br ejection for 14.5% of the initial nPB on average over the troposphere, while the self-reaction accounts for a minimal 0.06% due to the low concentration of RO_2 compared to other reactants and to the second-order dependence on RO_2. An additional 3.9% of initial nPB ejects Br after H abstraction at the first carbon, followed by 1-$C_3H_6BrO_2$ reaction with HO_2, followed by photolysis of the short-lived $CH_3CH_2CHBrOOH$ product to yield the same radical as from 1-$C_3H_6BrO_2$ reaction with NO or itself. Thus, on average in the troposphere, 18.5% of the nPB ejects Br after only one OH reaction step. Only reactions of 1-$C_3H_6BrO_2$ with HO_2 or NO_2 followed by OH abstraction of the remaining H from the first carbon lead to production of bromopropionaldehyde (CH_3CH_2CBrO), and the HO_2 channel accounts for slightly less than 1.2% of the original nPB, while the NO_2 channel accounts for 0.04%, giving a tropospheric average yield of 1.2% CH_3CH_2CBrO from nPB.

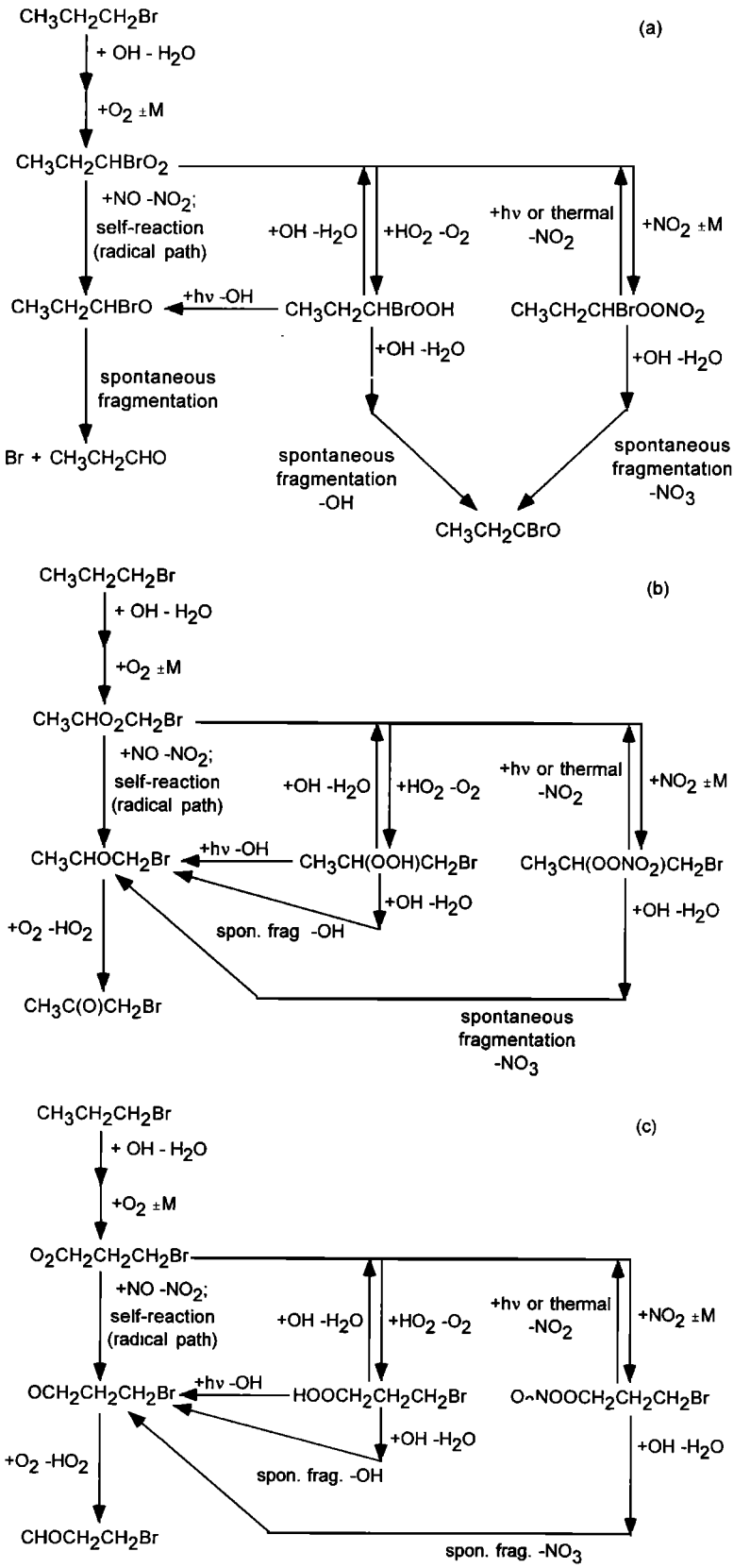


Figure 1. Illustrations of OH reactions and possible products for nPB and an example oxidation product. (a) nPB + OH reaction at first (brominated) carbon, (b) nPB + OH reaction at second carbon, (c) nPB + OH reaction at third carbon, (d) photolysis and reaction of OH at the aldehyde H of a sample aldehyde degradation product, 3-bromopropionaldehyde, and its products ("further reactions" indicates reactions of the RO_2 produced with NO, NO_2, HO_2, OH, and O_2 in similar manner to the reactions of $C_3H_6BrO_2$ radicals in Figures 1a, 1b, and 1c to produce stable degradation products or to eject Br).

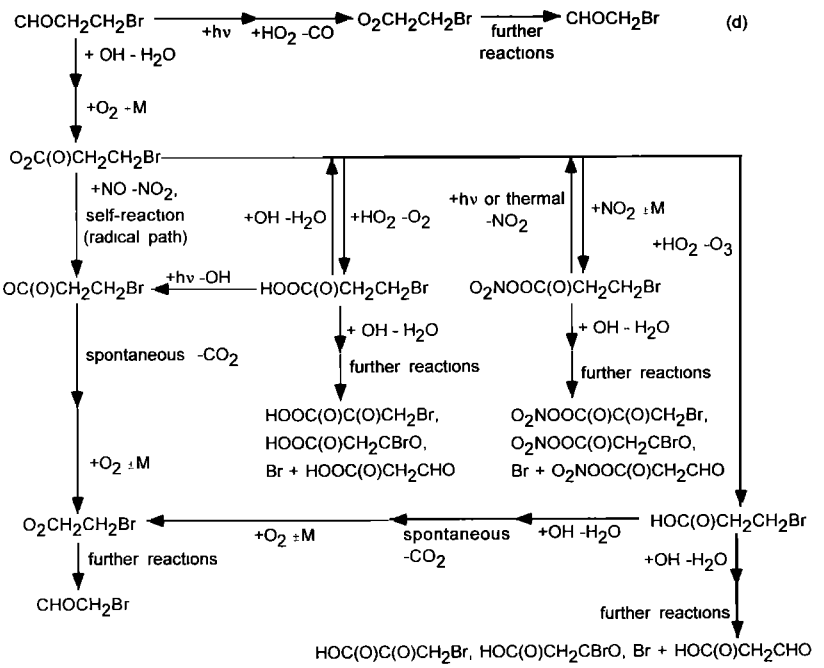


Figure 1. (continued)

3.2. Loss Processes of Radicals and Degradation Products

The reactions of the various compounds produced by nPB oxidation, including those of the various RO_2 radicals, the shorter-lived intermediate compounds such as alkyl hydroperoxides and peroxynitrates, and the longer-lived degradation products, have not generally been studied in the laboratory to date. The possible outcomes and products of reaction can become complicated, such as is illustrated in Figure 1d for the OH abstraction of the aldehyde H from 3-bromopropionaldehyde, the primary degradation product illustrated in Figure 1c. It must be noted, however, that many oxidation or photolysis steps are required; all nPB degradation products that are not removed by dry or wet deposition ultimately release Br to the atmosphere. Reaction rate constants of degradation products with OH are estimated by the structure-activity relationship of *Kwok and Atkinson* [1995]. Other rate constants, such as those of the RO_2 radical reactions, are taken as the rate constants of analogous reactions listed in at least one of the atmospheric chemistry evaluations [*Atkinson et al.*, 1997; *DeMore et al.*, 1997] in this study. Photolysis rates for the oxidation products are also taken as those of analogous compounds (e.g., $CH_3C(O)CH_2Br$ represented by acetone) based on the Atkinson et al. or DeMore et al. evaluations. The reaction rate constants used are listed in Table 1 and are discussed in detail below.

Many of the longer-lived degradation products are also potentially subject to wet deposition, but parameters including mass accommodation coefficients incorporated in the calculation of their rate of removal have not yet been measured. The rainout rate constants for all of the organic degradation products are treated as first-order parameterizations based on the mass accommodation coefficients of analogous compounds on liquid water [*DeMore et al.*, 1997]. For BrAc, which is based on the acetone mass accommodation coefficient, this results in a rainout rate about two thirds that of nitric acid. These rainout parameters, which neglect saturation of rainwater with the degradation products on the basis that their concentrations are probably lower than the solubility limit for any expected nPB emission rate, are our best estimate and are called the "α-based" rainout case below. To illustrate the sensitivity of bromine loading by nPB to rainout, additional studies used rainout coefficients identical to that of nitric acid for the nPB degradation products ("high" rainout case).

3.3. RO_2 + NO Reactions

We consider only the major path, $RO_2 + NO \rightarrow RO + NO_2$. The rate constant is at least 5.0×10^{-12} cm^3 molecules^{-1} s^{-1} at 298 K for $R = CH_3$, C_2H_5, 1-C_3H_7, or 2-C_3H_7, increases to 1.1×10^{-11} cm^3 molecules^{-1} s^{-1} at 298 K for $R = CH_2Br$, and is 2.0×10^{-11} cm^3 molecules^{-1} s^{-1} at 298 K for $R = CH_3C(O)$ and $C_2H_5C(O)$ [*Atkinson et al.*, 1997]. For $R = CH_3$, C_2H_5, CH_2Br, and $CH_3C(O)$ the rate constants are observed to increase weakly with decreasing temperature, proportional to exp $(300/T)$ to within experimental uncertainty [*DeMore et al.*, 1997]. We use the CH_2BrO_2 + NO rate constant expression of *DeMore et al.* [1997] for 1-bromo-1-dioxy radicals and the exp $(300/T)$ temperature dependence with the 298 K measurements recommended by *Atkinson et al.* [1997] for the two $C_3H_7O_2$ + NO radical isomers and for $CH_3C(O)$ and $C_2H_5C(O)$ to represent other bromodioxy or bromoacyldioxy radical rate constants, respectively, to give the preexponential factors for Table 1. A minor (up to 4% at 298 K, one atmosphere pressure for 2-$C_3H_7O_2$) additional pathway has been observed for alkyl radicals that results in $RONO_2$ [*Atkinson et al.*, 1997]. Because $RONO_2$ for R up to C_3H_7 have significant absorption cross sections at wavelengths longer than 300 nm and probably have unit photodissociation quantum yield [*Atkinson et al.*, 1997], any $RONO_2$ formed is expected to photolyze rapidly during the day, so that this minor product is not considered in this study.

Table 1. Estimates of Reaction Rate Constants and Mass Accommodation Coefficients for the Degradation Chemistry of n-Propyl Bromide

Reaction[a]	Rate Constant in Appropriate Units[b] or Analogous Compound	Reference
$CH_3CH_2CH_2Br + OH \rightarrow CH_3CH_2CHBrO_2 + H_2O$		*Kwok and Atkinson* [1995] distribution; *Nelson et al.* [1997] total
$CH_3CH_2CH_2Br + OH \rightarrow CH_3CH(O_2)CH_2Br + H_2O$		
$CH_3CH_2CH_2Br + OH \rightarrow O_2CH_2CH_2CH_2Br + H_2O$		
$RCHBrO_2 + NO \rightarrow Br + RCHO + NO_2$	$4.0 \times 10^{-12} \exp(300/T)$	*DeMore et al.* [1997] for T dependence; *Atkinson et al.* [1997] for preexponential factors
$RXCHO_2 + NO \rightarrow RXCO + NO_2 + HO_2$[c]	$1.8 \times 10^{-12} \exp(300/T)$	
$XC(O)O_2 + NO \rightarrow X + CO_2 + NO_2$	$7.3 \times 10^{-12} \exp(300/T)$	
$XO_2 + NO_2 + M \rightarrow XOONO_2 + M$	three body[d] with $k_0 = 1.3 \times 10^{-29}(T/300)^{-6.2}$ $k_\infty = 8.8 \times 10^{-12}$ $g = 0.31$	*Atkinson et al.* [1997]
$XC(O)O_2 + NO_2 + M \rightarrow XC(O)OONO_2 + M$	three body[d] with $k_0 = 2.7 \times 10^{-28}(T/300)^{-7.1}$ $k_\infty = 1.2 \times 10^{-11}(T/300)^{-0.9}$ $g = 0.30$	*Atkinson et al.* [1997]
$XOONO_2 \rightarrow XO_2 + NO_2$	$9 \times 10^{15} \exp(-10{,}450/T)$	*Atkinson* [1994]
$XC(O)OONO_2 \rightarrow XC(O)O_2 + NO_2$	$4 \times 10^{16} \exp(-13{,}600/T)$	*Atkinson* [1994]
$2R_1R_2CBrO_2 \rightarrow 2R_1C(O)R_2 + 2Br + O_2$	3.3×10^{-11}	*Atkinson et al.* [1997]
$2RXCHO_2 \rightarrow 2RC(O)X + O_2 + 2HO_2$[c]	3.9×10^{-12}	*Atkinson et al.* [1997]
$2XC(O)O_2 \rightarrow 2X + 2CO_2 + O_2$	$2.9 \times 10^{-12} \exp(500/T)$	*DeMore et al.* [1997]
$XOOH + OH \rightarrow XO_2 + H_2O$	$2.66 \times 10^{-12} \exp(200/T)$	*DeMore et al.* [1997]
$RXCHOOH + OH \rightarrow RC(O)X + OH + H_2O$	$3.8 \times 10^{-13} \exp(200/T)$	
$XCH_2OOH + OH \rightarrow XCHO + OH + H_2O$	$7.6 \times 10^{-13} \exp(200/T)$	
$XC(O)OOH + OH \rightarrow XC(O)O_2 + H_2O$	$2.66 \times 10^{-12} \exp(200/T)$	
$XC(O)OH + OH \rightarrow X + CO_2 + H_2O$	$3.0 \times 10^{-13} \exp(255/T)$	*Kwok and Atkinson* [1995]; section 3.11 of text
OH + XCHO, RCBrO, $CH_3C(O)CH_2Br$, $XC(O)OONO_2$, as well as OH + XC(O)OH or XC(O)OOH at H along X		*Kwok and Atkinson* [1995]
Photolysis reactions		
$CH_3CH_2CH_2Br + h\nu$	$CH_3Br + h\nu$	*DeMore et al.* [1997]
$CH_3C(O)CH_2Br + h\nu$	$CH_3C(O)CH_3 + h\nu$	*Gierczak et al.* [1998]
$CH_3CH_2CBrO + h\nu$, $CHOCH_2CH_2Br + h\nu$, $CHOCH_2CBrO + h\nu$, $ZCOCH_2CBrO + h\nu$	$CH_3CH_2CHO + h\nu$	*Atkinson et al.* [1997]
$CHOC(O)CH_2Br + h\nu$, $CH_3C(O)CBrO + h\nu$, $CHOC(O)CBrO + h\nu$, $ZC(O)C(O)CH_2Br + h\nu$, $ZC(O)C(O)CBrO + h\nu$	$CH_3C(O)CHO + h\nu$	*Atkinson et al.* [1997]
$CHOCBrO + h\nu$, $ZC(O)CBrO + h\nu$	$CHOCHO + h\nu$	*Atkinson et al.* [1997]
$XOOH + h\nu$, $XC(O)OOH + h\nu$ except when X contains adjacent C=O	$CH_3OOH + h\nu$	*DeMore et al.* [1997]
$XOONO_2 + h\nu$, $XC(O)OONO_2 + h\nu$ except when X contains adjacent C=O	$CH_3C(O)OONO_2 + h\nu$	*DeMore et al.* [1997]
Mass accommodation coefficients for "α-based" rainout		
$CH_3C(O)CH_2Br$	$CH_3C(O)CH_3$	*DeMore et al.* [1997]
XCHO	CH_3CH_2CHO (3-carbon) or CH_3CHO (2-carbon)	*DeMore et al.* [1997]
RCBrO	0.0	
XC(O)OH	$CH_3C(O)OH$	*DeMore et al.* [1997]
XOOH	CH3OOH	*DeMore et al.* [1997]
XC(O)OOH	$CH_3C(O)OOH$	*DeMore et al.* [1997]
$XOONO_2$	$CH_3C(O)OONO_2$	*DeMore et al.* [1997]
$XC(O)OONO_2$	$CH_3C(O)OONO_2$	*DeMore et al.* [1997]
CHOC(O)CBrO	CHOCHO	*Schweitzer et al.* [1998]
XO_2 and other radicals	0.0	

[a]R, R_1, R_2 = alkyl group not containing Br; X = brominated alkyl group; Z = OH, OOH, or $OONO_2$.

[b]"Appropriate units": s^{-1} for photolysis or first-order thermal decomposition, cm^3 molecules^{-1} s^{-1} for second-order reactions or third-order reactions (including the $k_0[M]$ low-pressure terms). T is in K, [M] is in molecules cm^{-3}.

[c]An additional O_2 not shown on the left side reacts instantly with the initially formed radical to produce HO_2 (see section 3.7).

[d]"Three-body" rate constant given by the Troe expression, $k = k_0[M]k_\infty 10^f(k_0[M] + k_\infty)^{-1}$ with $f = \log_{10}(g)(1 + [\log_{10}(k_0[M]/k_\infty)]^2)^{-1}$.

3.4. RO_2 + HO_2 Reactions

We use the *DeMore et al.* [1997] $C_2H_5O_2$ + HO_2 rate constant as an approximation for all RO_2 + HO_2 rate constants. However, the possibility that the temperature dependence becomes stronger with increasing size of R as is indicated by the *Atkinson et al.* [1997] recommendation for $C_2H_5O_2$ + HO_2 compared to CH_3O_2 + HO_2 should be noted.

The acetylperoxy radical $CH_3C(O)O_2$ reacts with HO_2 by two channels for temperatures of 260 to 340 K [*Atkinson et al.*, 1997], one producing $CH_3C(O)OOH$ + O_2 and the other producing $CH_3C(O)OH$ + O_3. The rate constants for the two channels as given in Table 1 are produced by first-order polynomial fits of ln $((1 - f)k_{tot})$ to $1/T$ and of ln (fk_{tot}) to $1/T$ at 260, 270, ..., 340 K from the total rate constant k_{tot} and fraction producing $CH_3C(O)OH$ + O_3, f, as reported by Atkinson et al. These rate expressions are used as estimates for all $RC(O)O_2$ + HO_2 reactions below.

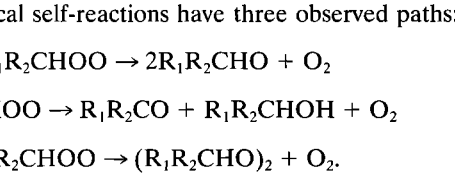
3.5. RO_2 + NO_2 Reaction and $ROONO_2$ Thermal Decomposition

The three-body RO_2 + NO_2 reaction produces peroxynitrates, $ROONO_2$. Acyl peroxynitrates $RC(O)OONO_2$ are fairly stable against thermal degradation and thus must be considered as possible Br carriers. However, the alkyl peroxynitrates are expected to be unstable against thermal decomposition in much of the troposphere; only in the upper troposphere would they be significant.

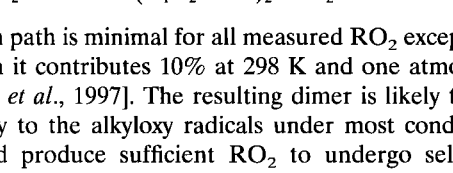
Rate constants in the Troe expression form are taken from *Atkinson et al.* [1997] for RO_2 + NO_2 three-body reactions for R = $CH_3C(O)$, CH_3, and C_2H_5. *DeMore et al.* [1997] provides recommendations for R = $CH_3C(O)$ and R = CH_3 which are in agreement to within the stated uncertainty with those of *Atkinson et al.* [1997] for troposphere-relevant temperatures and pressures. We use the R = $CH_3C(O)$ rate constant to estimate acylperoxy + NO_2 reaction rate constants and R = C_2H_5 for alkylperoxy + NO_2 reaction rate constants below. The first-order thermal decomposition rate constants in Table 1 are taken from the high-pressure limits given by *Atkinson* [1994] for $RC(O)OONO_2$ and $ROONO_2$.

3.6. RO_2 Self-Reactions

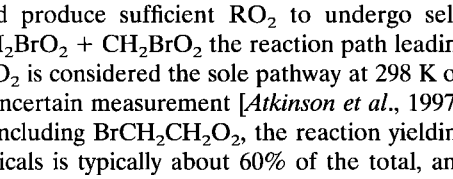
The RO_2 radical self-reactions have three observed paths:



$$2R_1R_2CHOO \rightarrow 2R_1R_2CHO + O_2$$



$$2R_1R_2CHOO \rightarrow R_1R_2CO + R_1R_2CHOH + O_2$$



$$2R_1R_2CHOO \rightarrow (R_1R_2CHO)_2 + O_2.$$

The dimerization path is minimal for all measured RO_2 except CH_3O_2, in which it contributes 10% at 298 K and one atmosphere [*Atkinson et al.*, 1997]. The resulting dimer is likely to photolyze rapidly to the alkyloxy radicals under most conditions that would produce sufficient RO_2 to undergo self-reaction. For CH_2BrO_2 + CH_2BrO_2 the reaction path leading to $2CH_2BrO$ + O_2 is considered the sole pathway at 298 K on the basis of an uncertain measurement [*Atkinson et al.*, 1997]. For other RO_2 including $BrCH_2CH_2O_2$, the reaction yielding two alkyloxy radicals is typically about 60% of the total, and that yielding alcohol and aldehyde (or ketone) is about 40% of the total reaction rate at 298 K [*Atkinson et al.*, 1997; *DeMore et al.*, 1997]. However, the alcohols oxidize with short lifetimes to the same aldehyde or ketone as results from the radical path. We thus combine the alcohol path with the radical path in this analysis. We use the CH_2BrO_2 and $BrCH_2CH_2O_2$ self-reaction rate constants at 298 K as reported by *Atkinson et al.* [1997] as upper-limit approximations for the RO_2 radical self-reaction rate constants encountered in the analysis. Errors due to these estimates are likely to be controlled by low RO_2 concentrations compared to other reactants.

As with α-bromoperoxy radicals, peroxyacyl radicals $RC(O)O_2$ are expected to produce only radical products on self reaction, which then decompose rapidly to R radical plus CO_2. The only recommendation is for $CH_3C(O)O_2$ self-reaction [*Atkinson et al.*, 1997; *DeMore et al.*, 1997], and we adopt the DeMore et al. rate constant for all $RC(O)O_2$ self-reactions.

3.7. RO Reactions

In accord with the discussion of *DeMore et al.* [1997] for the reaction of CH_2BrO_2 with NO, α-bromoalkoxy radicals are taken as unstable against dissociation to Br atom plus the aldehyde or ketone. Other RO radicals produced in nPB oxidation may degrade either by reaction with O_2 or by spontaneous fragmentation. The O_2 reaction to produce aldehyde or ketone plus HO_2 dominates in tropospheric conditions for most other small-chain RO radicals [*Atkinson et al.*, 1997] except β-hydroxyalkoxy, which rapidly produces a hydroxyalkyl radical and a ketone or aldehyde (and which could be produced from nPB degradation only if alcohols were produced, then oxidized at C not adjacent to the alcohol OH group). Three-body combination with NO_2 produces a nitrate that will regenerate RO on photolysis, so this reaction is not considered.

3.8. ROOH Reactions

The fastest reaction of this short-lived reservoir is reaction with OH at either the peroxy H, which regenerates RO_2, or a peroxyalkyl H, which results in a radical which spontaneously ejects OH to leave a ketone or aldehyde. Abstractions of H at alkyl sites not bound to the peroxy substituent are likely to be negligible compared to the peroxy and peroxyalkyl sites, and these are not considered in the figures. Our estimates for OH reaction rate constants with alkyl hydroperoxides given in Table 1 are based on the CH_3OOH + OH recommendation of *DeMore et al.* [1997], with which the *Atkinson et al.* [1997] recommendation for this reaction agrees to within reported uncertainty. While peroxycarboxylic acids $RC(O)OOH$ lack a peroxyalkyl H, abstraction at the peroxyacid H is still a fast reaction in many cases compared with any H abstraction on the alkyl chain. We nonetheless consider both the H-OO abstraction (estimated by the H-OO reaction rate constant for CH_3OOH) and the H abstraction rates on the alkyl chain for peroxycarboxylic acids below. The other reaction available to hydroperoxides or peroxycarboxylic acids, photolysis, is likely to yield the same alkoxy radical as is produced by the RO_2 + NO reaction.

3.9. Photolysis of Carbonyl Compounds

Aldehyde and bromoaldehyde (RCBrO) photolysis cross sections and quantum yields are taken as those of propionaldehyde (CH_3CH_2CHO) for three-carbon compounds or as those of acetaldehyde (CH_3CHO) for two-carbon compounds. $BrAc(CH_3C(O)CH_2Br)$ photolysis is treated as that of acetone ($CH_3C(O)CH_3$). However, cross sections of conjugated dicarbonyl compounds such as $CH_3C(O)CBrO$ are taken as those of methylglyoxal ($CH_3C(O)CHO$) because these compounds are

Table 2. Two-Dimensional n-Propyl Bromide Model Scenarios[a]

Flux Scenario	nPB Deg.?	Rainout	τ_{nPB}, days	ODP	Burden in 10^{30} molecules: Strat. ΔBr_y	Strat. Total[b]	20°S–20°N L.A.T. total[b]	20°S–20°N Total[b] X-Tropo Flux
Global	no; nPB + Cl		19.0	0.0292	47.2	51.7	1.42	0.639
Global	no		19.5	0.0289	46.1	52.5	1.47	0.649
30°–60°N	no		19.0	0.0157	22.8	29.3	0.51	0.245
5°S–30°N	no		9.2	0.0379	65.2	68.0	2.71	1.193
Global	yes	α-based	19.3	0.0394	70.3	79.7	2.45	1.072
Global	yes	high	19.3	0.0245	45.0	53.5	1.51	0.640
30°–60°N	yes	α-based	18.5	0.0195	35.4	45.2	0.99	0.463
30°–60°N	yes	high	18.5	0.0108	20.7	29.5	0.52	0.239
5°S–30°N	yes	α-based	9.0	0.0550	102.4	107.1	4.30	1.861
5°S–30°N	yes	high	8.9	0.0344	65.4	69.2	2.76	1.164

[a]Abbreviations for table heading: deg., degradation; strat., stratospheric; L.A.T., layer above tropopause; x-tropo flux, cross-tropopause flux (in units of 10^6 molecules cm^{-2} s^{-1}).
[b]Total equal to nPB + RBr + ΔBr_y.

likely to photolyze strongly at near-ultraviolet to visible wavelengths. Data for propionaldehyde, acetaldehyde, acetone, and methylglyoxal photolysis are taken from *Atkinson et al.* [1997].

3.10. $ROONO_2$ Reactions

Unlike peroxyacyl nitrates, alkyl peroxynitrates decompose quickly at high temperatures, regenerating RO_2 + NO_2 [*Atkinson*, 1994]. Photolysis is also expected to regenerate RO_2 + NO_2, but the alternate photolysis products RO + NO_3 have not conclusively been ruled out by measurement. Abstraction of H from the peroxyalkyl site by OH is also possible as with the hydroperoxide ROOH, and the resulting radical will probably decompose to a ketone or aldehyde plus NO_3. As with ROOH, H abstraction at sites other than the peroxy site is likely to be negligible for alkyl peroxynitrates. Abstraction of H atoms from the alkyl carbons of acyl peroxynitrates may occur and is accounted for by the *Kwok and Atkinson* [1995] structure-activity relationship.

3.11. RC(O)OH Reactions

The temperature dependence of OH addition to COOH groups is not given by *Kwok and Atkinson* [1995]. We estimate this rate constant by subtracting the Atkinson method $F(COOH)k_{pri}$ from the CH_3COOH + OH rate constant expression given by *DeMore et al.* [1997], 4.0×10^{-13} exp $((200 \pm 400)/T)$ cm^3 $molecules^{-1}$ s^{-1}, and fitting the natural log of that difference to a line in $1/T$. The resulting expression in Table 1 should be valid to within a factor of 2 in most cases, although its temperature dependence should be regarded as highly uncertain. An estimate for the C_2H_5COOH + OH rate constant based on this $k_{COOH+OH}$ and the Atkinson method for the alkyl chain is consistently high by more than 50% compared to the value given by *Atkinson et al.* [1997], but has a minimal temperature dependence as does the literature value.

4. Two-Dimensional Model Studies

The two-dimensional nPB model simulations were undertaken with a set of different conditions as listed in Table 2 in order to evaluate the importance of several variables likely to affect bromine loading. Unlike our past studies [*Wuebbles et al.*, 1998, 1999a], in which a constant global mixing ratio of nPB is fixed as the surface boundary condition, each of these simulations uses a surface rate of nPB emission, and these studies are designed so that their global total rate of nPB emission is 2.2 Tg yr^{-1}, or a surface flux of 6.7×10^7 molecules cm^{-2} s^{-1} over the globe, in order to facilitate comparisons of brominated species loading among them. We first examine the differences between our past work [*Wuebbles et al.*, 1998, 1999a] and the most consistent current simulation. Then, we consider the effects of the variables on the ozone effect of nPB in our two-dimensional model. The first variable considered is flux location, in which the global emission profile for nPB is replaced first by the best representation of the more likely region for use of a replacement compound, the industrial region of the Northern Hemisphere (30°–60°N), that can be achieved within the constraints of a zonal mean model; then, by a tropical emission (5°S–30°N) intended to illustrate the maximum ozone effect expected from nPB. Second, we introduce the nPB degradation chemistry to our two-dimensional model and compare ozone effects with our nondegradation studies. Third, we consider the changes in the ozone effects achieved in the nPB degradation chemistry due to a high rainout scenario (as discussed in section 3.2 above). Finally, we indicate uncertainties associated with the nPB degradation chemistry and what their potential effects could be on nPB ozone effects.

The first three columns of Table 2 identify our two-dimensional model scenarios. The first indicates the latitude range over which nPB emissions occur: "global," "30°–60°N," or "5°S–30°N" as indicated above. The second column identifies whether nPB degradation chemistry is included. "Yes" in this column signifies that nPB oxidation proceeds to products as illustrated in Figures 1a, 1b, and 1c and that those products undergo further oxidation steps or photolysis to eventually release inorganic bromine unless they are removed from the troposphere by dry or wet deposition, while "no" indicates that the nPB + OH reaction is treated as immediately releasing inorganic bromine, as was done in our previous studies [*Wuebbles et al.*, 1998, 1999a]. When nPB degradation chemistry applies, the third column indicates the choice of rainout parameters for nPB degradation products between "α-based" (predicted from mass accommodation coefficients for analogous compounds on water) and "high" (similar to nitric acid) as discussed in section 3.2. The fourth column shows the nPB global lifetime against chemical reaction, defined as the total burden of nPB divided by the total rate of chemical degrada-

tion of nPB over the entire model domain for 1 model year. The fifth column gives the Ozone Depletion Potential of nPB, defined as the global average decrease in ozone column for a mass of nPB emitted divided by the global average decrease in ozone column for that same mass of CFC-11 [*Wuebbles*, 1981, 1983; *WMO*, 1992]. The sixth, seventh, and eighth columns list the total number of molecules of bromine-containing species (burden) due to the presence of nPB in the model (burden of brominated species in the nPB case minus burden of brominated species in the non-nPB "reference" model), summed over the model region noted and averaged over the model year. In the non-nPB reference model, burdens for nPB and all of its degradation products are zero, and burdens of nPB degradation products are also zero in the nPB-perturbed model scenarios that do not use the degradation chemistry. The sixth column provides the burden change from the model tropopause to the top of the atmosphere for inorganic bromine compounds alone, the seventh gives the burden change from the model tropopause to the top of the atmosphere for nPB plus its organic degradation products plus inorganic bromine, and the eighth gives the burden change for nPB plus organic degradation products plus inorganic bromine within the model for the 1.5 km log-pressure layer immediately above the tropopause at the tropical latitudes 20°S to 20°N. The ninth column gives the positive definite upstream difference flux of nPB plus organic degradation products plus inorganic bromine perturbation across the model tropopause for 20°S to 20°N. The last three columns will be tested for correlation with ODP as part of section 6 below.

4.1. Comparison With *Wuebbles et al.* [1998, 1999a]

The study in Table 2 most consistent with those of *Wuebbles et al.* [1998, 1999a], but not identical due to the boundary condition revision, is that with a global nPB flux, no degradation chemistry, but including the nPB + Cl reaction of *Donaghy et al.* [1993]. The ODP calculated for this case, 0.029, is slightly higher than we found in the work of *Wuebbles et al.* [1999a]. However, the atmospheric lifetime (defined as total atmospheric burden of nPB divided by total chemical rate of destruction of nPB) in the current study of 19.0 days is greater than the 10-day value reported in the previous work. As will be discussed below in comparison of nPB lifetimes for the tropical-flux study to the global- and industrial-flux studies, this is primarily an effect of the selection of a constant-flux boundary condition in the current study instead of a constant mixing ratio as in the previous study.

A consideration for the purposes of the other simulations is the effect of the nPB + Cl reaction reported by *Donaghy et al.* [1993] on ozone in the model. Comparison of rows 1 and 2 of Table 2, in which the global-flux, no degradation chemistry simulations with and without Cl reaction are compared, show that the inclusion of the Cl reaction has little effect on atmospheric lifetime, Ozone Depletion Potential (ODP), or brominated species perturbations and fluxes (to be further discussed below) in our model. Because we are unaware of a structure-activity relationship for H abstraction from alkanes which incorporates a temperature dependence, we chose to omit the nPB + Cl reaction for the remainder of the simulations.

4.2. Effect of nPB Flux Location

The flux cases labeled "global" represent an equal rate of nPB emission per unit area at all latitudes. Flux cases labeled "30°–60°N" and "5°S–30°N" indicate emissions only over those latitude ranges, and the flux levels used in the latitude-constrained scenarios have been increased by a constant factor per unit area in order to achieve the same global total flux of nPB as in the global emission scenario, 2.2 Tg nPB yr^{-1}. The "30°–60°N" scenario is intended to represent the most likely practical scenario for the use of nPB as a replacement compound: emissions throughout the industrialized Northern Hemisphere. This scenario is as consistent as practical in a two-dimensional model with the MOZART2 three-dimensional model studies for "North America, Europe, China, and Japan" emissions to be discussed below. The second flux case "5°S–30°N" is intended to represent the likely "worst-case" scenario for use of nPB: massive use of the replacement compound in tropical regions where convective transport could quickly send a larger fraction of nPB, degradation products, and troposphere-released inorganic bromine into the stratosphere. These scenarios are most comparable to the "India, Southeast Asia, and Indonesia" emissions case with MOZART2 discussed later in this paper.

The primary transport of short-lived compounds to the stratosphere is expected to occur through the tropical tropopause. The expected effect for the "30–60°N" scenario compared to a global scenario is that bromine perturbation from nPB would be required to travel farther on average, and through more opportunities for dry and wet deposition, in order to reach the stratosphere than is the case for the global flux scenario. Conversely, the "5°S–30°N" scenario should provide less opportunity for removal of nPB-generated bromine perturbations before they can reach the stratosphere compared to the "global" scenario. Both in the absence and in the presence of the nPB degradation chemistry discussed below, our two-dimensional model indicates an effect of emissions location as expected: the nPB ODP is reduced by essentially a factor of 2 in the "30°N–60°N" cases versus their "global" counterparts despite little lifetime effect, and ODPs, brominated species burdens, and brominated species fluxes all increase by some 50% with a factor of 2 decrease in lifetime in the "5°S–30°N" cases versus "global."

The fact that the nPB lifetime is affected little in the "30°N–60°N" no-degradation case compared to the global no-degradation case without Cl reaction, but is reduced to a value comparable to that in the work of *Wuebbles et al.* [1999a] in the "5°S–30°N" no-degradation case, allows us to explain the lifetime difference between the past and current studies. The use of a constant mixing ratio boundary condition in the past studies, combined with the fact that the local nPB lifetime in the tropics is 6 days compared to the global average of 19 as found in this study with constant flux boundary conditions, resulted in a considerable excess of nPB flux introduced in the tropics in order to maintain a consistent burden with extratropical latitudes. In the past studies the global lifetime was thus calculated with a considerable weighting toward the shorter-lived tropical nPB. We suspect that the excess flux of nPB in the past studies could have driven nonlinearities in the bromine chemistry, so that the ODPs in the past work were similar to those in the current global scenarios mostly by coincidence. The current, constant-global-flux simulations lack this excess of nPB in the tropics, so that the atmospheric lifetime calculated is weighted toward mid and high latitudes. We consider the current nPB lifetimes more likely to apply to possible future nPB emissions than those published by *Wuebbles et al.* [1998, 1999a].

Table 3. Lifetimes of nPB and Its Degradation Products, Maximum and Average Degradation Product Concentration in the Troposphere As a Fraction of Local nPB From the Two-Dimensional Model ("α-Based" Rainout, Global Flux Degradation Case), and Tropospheric Average Production Rates for Degradation Products As Percent of nPB Degradation Rate

nPB or Degradation Product	Chemical Lifetime, days	Rainout Lifetime, days	Maximum Fraction, %	Average Fraction, %	Average Fraction of nPB Loss Rate, %
$CH_3CH_2CH_2Br$ (nPB)	19.3				
CH_3CH_2CBrO	1.2	9.3	0.46	0.09	1.2
$CH_3C(O)CH_2Br$	21.5	16.0	195	70.1	71.2
$CHOCH_2CH_2Br$	0.34	7.2	0.45	0.16	9.1
$CHOCH_2Br$	0.42	7.0	0.4	0.14	6.8
$CHOCH_2CBrO$	0.09	6.2	<0.01	<0.01	0.14
$CH_3C(O)CBrO$	0.07	6.8	0.03	<0.01	1.6
$CHOC(O)CH_2Br$	0.06	10.6	0.08	0.02	8.0
$HOC(O)CH_2CH_2Br$	3.9	7.7	1.8	0.51	2.0
$HOOC(O)CH_2CH_2Br$	1.2	6.3	0.31	0.1	1.3
$O_2NOOC(O)CH_2CH_2Br$	0.4	7.2	0.81	0.23	1.9
$CHOCBrO$	0.10	9.6	<0.01	<0.01	0.11
$CHOC(O)CBrO$	0.06	6.6	<0.01	<0.01	0.26
$HOC(O)C(O)CH_2Br$	0.07	7.0	0.02	<0.01	0.86
$HOOC(O)C(O)CH_2Br$	0.06	6.0	<0.01	<0.01	0.34
$O_2NOOC(O)C(O)CH_2Br$	0.04	6.0	0.02	<0.01	0.58
$HOC(O)CH_2Br$	7.7	10.6	7.1	1.8	4.4
$HOOC(O)CH_2Br$	1.3	6.8	0.72	0.18	2.0
$O_2NOOC(O)CH_2Br$	0.56	8.7	3.2	0.62	4.2
$HOC(O)CH_2CBrO$	0.94	9.9	0.04	<0.01	0.14
$HOOC(O)CH_2CBrO$	1.1	6.0	0.01	<0.01	0.069
$O_2NOOC(O)CH_2CBrO$	0.6	9.1	0.04	<0.01	0.12
$HOC(O)C(O)CBrO$	0.07	9.1	<0.01	<0.01	0.046
$HOOC(O)C(O)CBrO$	0.06	5.9	<0.01	<0.01	0.021
$O_2NOOC(O)C(O)CBrO$	0.05	8.5	<0.01	<0.01	0.035
$HOC(O)CBrO$	0.07	6.6	<0.01	<0.01	0.074
$HOOC(O)CBrO$	0.06	6.1	<0.01	<0.01	<0.01
$O_2NOOC(O)CBrO$	0.05	7.6	<0.01	<0.01	0.019

4.3. Effects of Degradation Chemistry

We incorporated the detailed oxidation chemistry of nPB as described above into our two-dimensional chemical-transport model, constituting 324 additional thermal reactions, 86 additional photolysis reactions, and 125 additional species. Of those 125 species, 27 of the nPB tropospheric oxidation products are relatively stable brominated species including aldehydes, ketones, carboxylic acids, acyl hydroperoxides, and acyl peroxynitrates. These species, their photochemical lifetimes and tropospheric rainout lifetimes in days, and the average and maximum concentrations achieved in the troposphere (as a percentage of the local nPB concentration) are listed in Table 3. Among the species considered, only BrAc ($CH_3C(O)CH_2Br$) is greater than 10% of the local nPB concentration on average over the troposphere, and indeed exceeds local nPB concentrations in the upper tropical troposphere. Figure 2 shows the annual average profile of percentage of BrAc with respect to nPB in comparison with the tropopause (dotted line) of the model. Analysis of degradation rates in the global-flux, α-based rainout degradation case shows that on average in the troposphere, 18% of the initial nPB reaction releases bromine directly. BrAc is slightly longer-lived than nPB, and its modeled rainout lifetime (total atmospheric burden of the degradation product divided by its total removal rate by dry plus wet deposition) is shorter than its chemical lifetime, unlike most other degradation products. On average over the model troposphere for the global-flux, α-based rainout degradation case, 86.7% of the BrAc promptly produces inorganic bromine (Br_y) on further reaction, a majority of this by photolysis. Only 2.2% produces $CH_3C(O)CBrO$, and 11.1% produces $CHOC(O)CH_2Br$, and each of these compounds rapidly photolyzes (see section 3.9 and Table 3) as its major reaction to release Br.

The presence of significant BrAc, which is of comparable chemical lifetime to nPB but rains out more slowly than Br_y, in

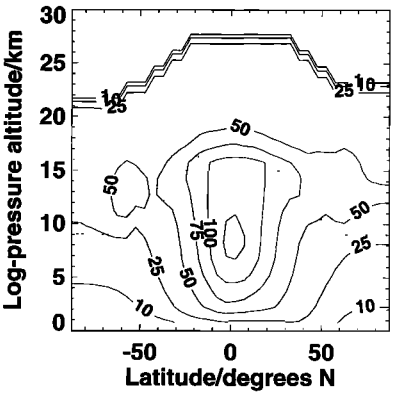


Figure 2. Annual-averaged BrAc local concentrations as a percentage of the concentration of nPB in the two-dimensional model (global flux, degradation case with rainout based on mass accommodation coefficients). The dotted line indicates the model tropopause.

our model simulations indicates that this compound may participate in transporting bromine to the stratosphere. A comparison of the degradation chemistry, α-based rainout cases with their nondegradation counterparts in Table 2 indicates that consideration of degradation chemistry does increase the stratospheric ozone effect of nPB in our model. The nPB chemical lifetime is not significantly perturbed by the introduction of degradation chemistry as expected because the OH effects of the degradation chemistry are negligible compared to the production and loss processes affecting OH in our "reference" model without nPB. However, the ODP for the reference "α-based" rainout case with degradation chemistry is some 30% greater than that without degradation for each flux case. This and the brominated species burden and cross-tropopause flux analysis in Table 2 show that stratospheric bromine from nPB in the two-dimensional model is increased by the inclusion of degradation chemistry. The bromine reaching the stratosphere, whether as nPB, as BrAc, other nPB degradation products, or as a perturbation in inorganic brominated species compared to our reference model, ΔBr_y, will be further discussed below.

Figure 2 illustrates that a significant fraction of nPB is oxidized to BrAc. Averaged over the troposphere, 71.2% of the nPB is converted to BrAc, as shown in Table 3. The fraction of the BrAc produced that is chemically reacted versus that which is removed by rainout and dry deposition can be determined from Table 3. For BrAc the chemical lifetime (global burden/global reaction rate) is 21.5 days, while the rainout lifetime (global burden/tropospheric removal rate) is 16.0 days. This provides a total BrAc lifetime of 9.2 days, from which we find that 57% of BrAc is rained out and 43% is chemically degraded on average.

The other compounds do not contribute significantly. While the degradation rate analysis suggests that some of the compounds in this model (such as the aldehydes $CHOCH_2CH_2Br$, $CHOCH_2Br$, and $CHOC(O)CH_2Br$) are produced at a rate more than 1% of the nPB degradation rate, the short lifetimes of many of those compounds convert them quickly to later degradation products, ultimately releasing inorganic bromine. The only degradation product other than BrAc with a fraction of local nPB concentration greater than 1% is bromoacetic acid ($HOC(O)CH_2Br$) at an average over the troposphere of 1.8% and a chemical lifetime of 7.7 days (see Table 3). However, since none of the lifetimes of nPB degradation products are greater than 1 month, and given a canonical time for exchange from the troposphere to the stratosphere of about 2 years, most of the nPB degradation products including BrAc will likely be oxidized further to ΔBr_y or rained out before reaching the stratosphere. This suggests a more compact chemistry scheme for use in the three-dimensional model MOZART2, in which only nPB, BrAc, and ΔBr_y are required to adequately represent the total nPB effects on stratospheric bromine.

4.4. Effects of Rainout Parameterization

The production of nPB degradation products that are more soluble in water than the original nPB suggests that some of the bromine from nPB may be removed in the troposphere through wet deposition of degradation products. However, the major degradation product, BrAc, is probably not as soluble as most of the inorganic acids (such as nitric acid or hydrogen chloride) or hydrogen peroxide, and many of the other degradation products are less soluble still (though many have much shorter chemical lifetimes than rainout lifetimes, so that removal by rainout is likely to be insignificant for these compounds). As a test of the uncertainty introduced by the dependence of degradation products on wet deposition, we ran separate model simulations with all degradation product wet deposition coefficients set identical to those for highly soluble species such as nitric acid (the "high" rainout cases in Table 2). These tests indicate that the ODP derived in the two-dimensional model is quite sensitive to degradation product rainout rates: the ODPs of the high rainout degradation cases are lower than the no-degradation ODPs for each of the flux conditions studied, and are slightly greater than half those of the "α-based" rainout degradation cases. Brominated species burdens and fluxes decrease similarly to the ODPs.

4.5. Uncertainties in Degradation Chemistry

Results from the degradation chemistry should be considered with the caveat that of all of the reactions and rainout rates involved, only the total rate constant for nPB + OH (not the distribution of RO_2 products by carbon atom) has been measured in the laboratory. The other reactions are based either on structure-activity relationships, particularly *Kwok and Atkinson* [1995] for OH reaction rate constants, or on reaction rate constants for analogous compounds (an approach used for all of the photolysis rate constants and most of the thermal rate constants). *Kwok and Atkinson* [1995] indicated that their predictions of OH reaction rate constants should be taken as valid to within a factor of 2; this should be considered a minimum estimate of error for other reactions included in the nPB degradation chemistry. Any minor RBr product is likely to contribute minimally unless an unexpectedly severe modification to the estimated rate constants for its production or degradation were required to correctly describe its chemistry. The primary concerns in this analysis thus involve the initial reaction of nPB with OH and the reactions and rainout of the major degradation product BrAc.

The initial nPB + OH reaction yields a tropospheric average of 71% BrAc because H abstraction at the second carbon is most favorable according to our application of *Kwok and Atkinson* [1995]. H abstraction at the first (brominated) carbon, which is responsible for all of the 1% CH_3CH_2CBrO produced plus essentially all of the 19% ejection of Br_y, is significantly less favorable. H abstraction at the third (methyl) carbon contributes only 9% of the nPB degradation in producing $CHOCH_2CH_2Br$. Photolysis, which is treated as that of methyl bromide, contributes about 0.01% of the nPB degradation in our analysis and can be neglected as a source of uncertainty unless the photodissociation cross sections or quantum yields for nPB prove unexpectedly larger than those for methyl bromide. If the true product fractions for H abstraction at the first and third carbon atoms were a factor of 2 higher and that at the second carbon were a factor of 2 lower than the estimates used above, the product distribution would have been considerably different: Br ejection would have increased to 40%, CH_3CH_2CBrO would have increased to 3%, and $CHOCH_2CH_2Br$ would have increased to 19% at the expense of BrAc, which would have decreased to 38%. Because the inorganic bromine compounds are likely to be more subject to rainout than BrAc, such a variation in nPB product yields would probably reduce stratospheric bromine loading.

Similarly, any hydrolysis or other heterogeneous reaction of BrAc could have the effect of reducing stratospheric bromine due to BrAc in favor of wet deposition of inorganic bromine reservoirs, as could a larger rainout rate than is suggested by the mass accommodation coefficient for acetone. Several

Table 4. Cross-Tropopause Fluxes Between 20°S and 20°N of n-Propyl Bromide, Bromoacetone, Other n-Propyl Bromide Degradation Products, and Inorganic Bromine Species Due to n-Propyl Bromide Perturbation for the Two-Dimensional Model Studies

			Fluxes in 10^3 molecules cm^{-2} s^{-1}				Percent of Total Flux			
Flux Scenario	nPB Deg.?	Rainout	nPB	BrAc	Other RBr	ΔBr_y	nPB	BrAc	Other RBr	ΔBr_y
Global	no; nPB + Cl		143			496	22.4			77.6
Global	no		153			496	23.6			76.4
30°–60°N	no		58.3			186.6	23.8			76.2
5°S–30°N	no		288			905	24.1			75.9
Global	yes	α-based	152	178	3.8	738	14.2	16.6	0.4	68.9
Global	yes	high	150	89	1.5	400	23.5	13.9	0.2	62.5
30°–60°N	yes	α-based	57.2	77.8	1.7	327	12.3	16.8	0.4	70.5
30°–60°N	yes	high	56.3	32.7	0.6	149.2	23.6	13.7	0.2	62.5
5°S–30°N	yes	α-based	284	305	6.7	1,266	15.2	16.4	0.4	68.0
5°S–30°N	yes	high	278	160	2.8	723	23.9	13.7	0.2	62.1

BrAc-associated uncertainties which could cause increased stratospheric bromine loading are associated with the primary BrAc tropospheric degradation mechanism, photolysis. The acetone photolysis cross sections and quantum yields are applied in this analysis; it is possible that the electron withdrawing effects of bromine cause a blue shift in the cross section of BrAc compared with acetone, which would inhibit its photolysis in the troposphere. Further, the effect of the bromine substitution on BrAc photolysis quantum yields is unknown: instead of the products assumed in this analysis, CH_3 + CH_2Br + CO (which amounts to bromine ejection), the molecular channel yielding CH_3CH_2Br + CO could be favored, producing another degradation product longer-lived than nPB. Laboratory measurement studies are needed in order to evaluate these concerns.

5. Bromine Reaching the Stratosphere From n-Propyl Bromide

5.1. Two-Dimensional Model Studies

A significant fraction of the chlorine or bromine loading in the stratosphere from short-lived gases can originate with chlorine or bromine released in the troposphere after reaction of the compound [e.g., *Ko et al.*, 1997]. In order to examine this effect in the case of nPB, we first compare the positive-definite, upstream difference-based advective fluxes of nPB, BrAc and other organic, bromine-containing degradation products (other RBr), and of change in inorganic bromine compounds between the nPB-perturbed simulation and a "reference" two-dimensional (2-D) simulation without nPB (ΔBr_y) across the tropopause between 20°S and 20°N to the total of all fluxes for

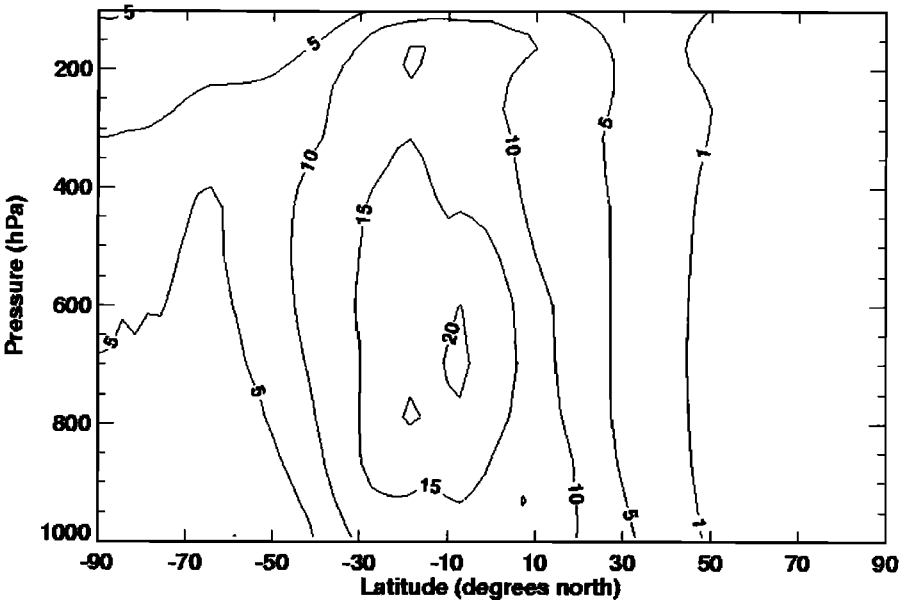


Figure 3. Zonally averaged OH concentrations for January from MOZART2 in units of 1×10^5 molecules cm^{-3}.

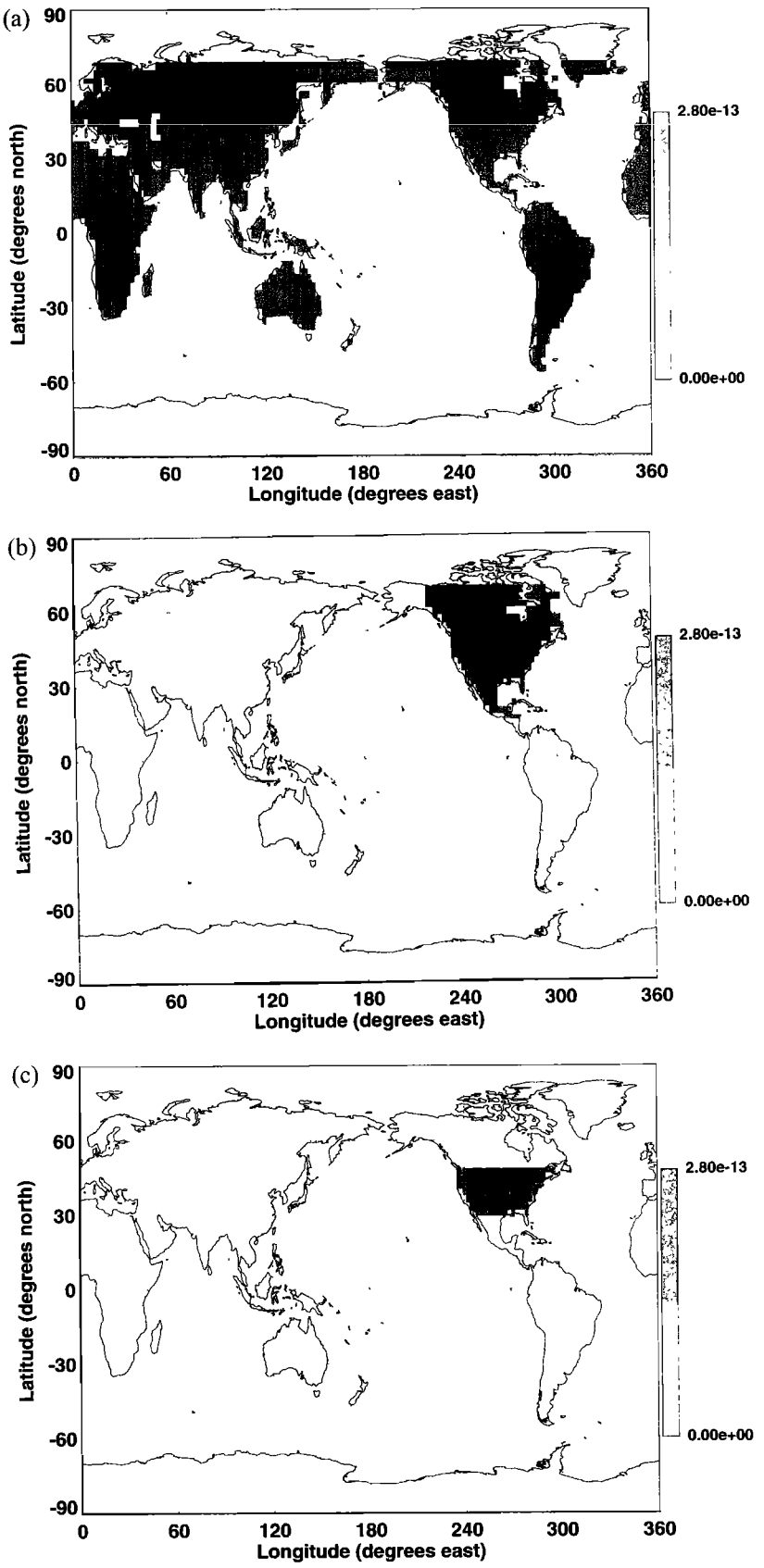


Figure 4. Location of surface emissions for the various scenarios used in the three-dimensional model: (a) global flux; (b) North America; (c) the contiguous United States; (d) North America, Europe, and Asia; and (e) India, Indonesia, and Southeast Asia. A constant land-only nPB surface flux of 2.776×10^{-13} kg m^{-2} s^{-1} was prescribed in each of the cases. No emissions were allowed north of 70°N or south of 60°S.

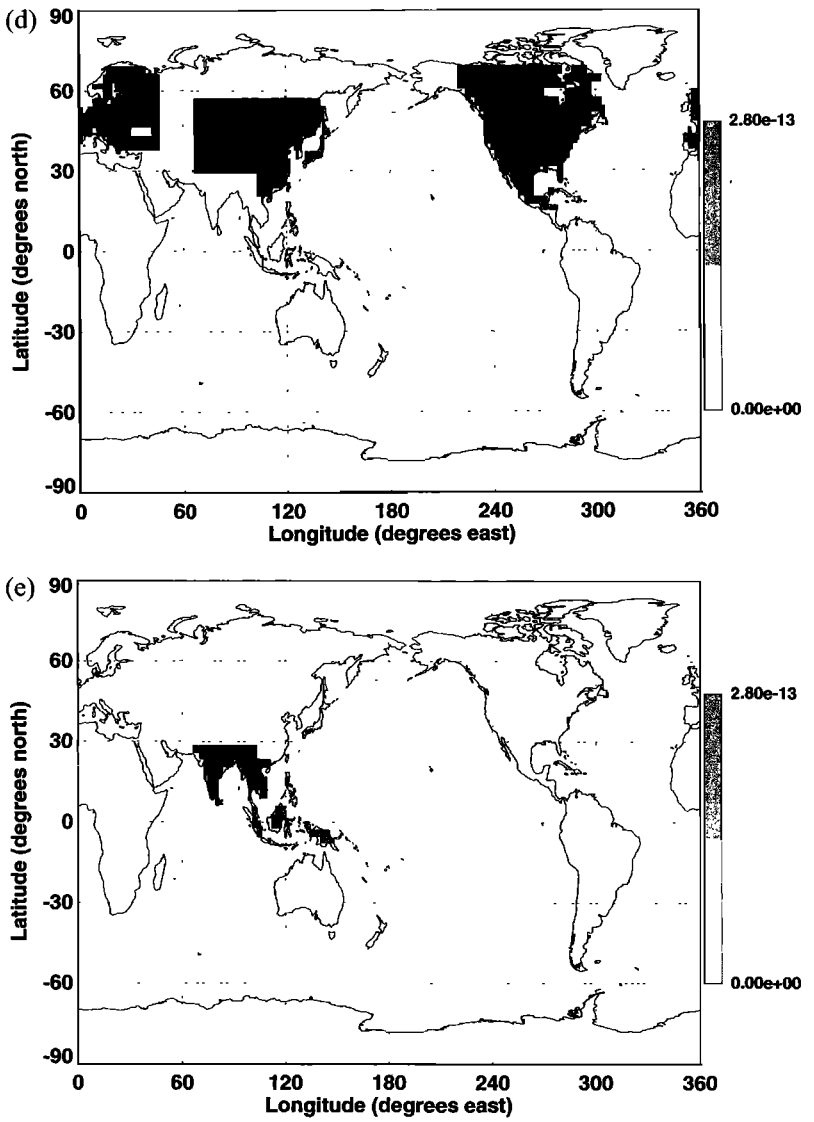


Figure 4. (continued)

each of the two-dimensional model runs in Table 4. The sum of these four fluxes appears as the last column of Table 2. The flux of nPB varies significantly only with respect to location of nPB emissions; neither presence or absence of degradation chemistry nor rainout scenario affect nPB flux. ΔBr_y, BrAc, and other RBr fluxes vary with emission latitude, qualitatively as do the nPB fluxes, but the ΔBr_y flux is enhanced considerably by inclusion of degradation chemistry. The upper limit rainout scenario, however, reduces fluxes of ΔBr_y, BrAc, and other RBr by almost a factor of 2. In no case is the contribution from RBr other than BrAc greater than 1%, but that of BrAc is slightly greater than that from nPB for each of the "α-based" rainout simulations. ΔBr_y is the majority of the total flux of brominated compounds in each model study. These results indicate that the findings of *Ko et al.* [1997] regarding the contribution of inorganic chlorine generated in the troposphere to the stratospheric ozone effects of short-lived chlorine species could be extremely significant for short-lived brominated gases, and also that the contribution of degradation products can be comparable to that from the original source gas.

5.2. Three-Dimensional Modeling Studies

It would be computationally prohibitive to include the full degradation scheme for nPB into the three-dimensional model. As suggested by the results discussed above, tests with the two-dimensional model indicated that the full scheme can be accurately reduced to consideration of the BrAc product and the change in reactive bromine, ΔBr_y. The inorganic brominated species produced through the reaction of nPB and its degradation products, such as Br, BrO, $BrONO_2$, HOBr, HBr, and BrCl, while treated explicitly in the 2-D model, are lumped as a change in Br_y in MOZART2. For this study, such an approach should be adequate because the primary purpose of using the three-dimensional model is to determine the amount of bromine reaching the stratosphere. The cross sections for photolysis of BrAc and its reaction rate with OH are the same as used in the two-dimensional model studies. However, upon reaction, BrAc is assumed to produce Br_y directly.

As nPB is primarily destroyed by reaction with the hydroxyl radical, globally accurate OH distributions are necessary for correctly calculating nPB distributions. Recently, *Spivakovsky*

et al. [2000] have combined hydroxyl measurements, the hydroxyl precursors O_3, H_2O, NO_y ($NO + NO_2 + 2N_2O_5 + NO_3 + HNO_2 + HNO_4$), CO, and hydrocarbons, and cloud optical depth with the HARVARD/Goddard Institute for Space Studies (GISS)/University of California, Irvine, (UCI) Chemical Tracer Model to calculate climatological distributions of OH. *Spivakovsky et al.* [2000] estimate their distributions to be globally accurate within ±15%, which establishes their data as the most accurate climatological distributions of OH available to date. Figure 3 depicts the zonally averaged January monthly mean OH concentrations from MOZART2, which were compared to corresponding results from *Spivakovsky et al.* [2000] (not shown). While the OH field is highly similar between the HARVARD model and MOZART2 north of 15°N, MOZART2 underestimates OH concentrations throughout the depth of the tropical troposphere and within the Southern Hemisphere. MOZART2 produces a maximum contour of about 20×10^5 molecules cm^{-3}, while the Spivakovsky et al. analysis produces a maximum contour of 25×10^5 molecules cm^{-3}. However, the locations of these maxima are similar. MOZART2 produces an OH distribution similar to that of *Spivakovsky et al.* [2000], except that MOZART tends to underestimate OH concentrations in the tropical latitudes and, to a lesser degree, to underestimate OH in the mid to high latitudes of the summer hemisphere.

The above results suggest scaling the MOZART2 OH field to yield a methyl chloroform tropospheric lifetime of 5.7 years would yield an OH distribution similar to that of *Spivakovsky et al.* [2000]. Scaling the OH field increases the hydroxyl radical concentrations to magnitudes well within the associated error of the *Spivakovsky et al.* [2000] distribution. The scaled MOZART2 OH distribution was used to determine the atmospheric distribution of nPB and its degradation products for several emissions cases as described below.

Owing to computational time restraints, only five emission scenarios were evaluated with the three-dimensional model. In each case the magnitude of the surface flux remained constant, and only land emissions were allowed, with location of emissions being the only variable. The first case involved the flux of nPB from all land surfaces north of 60°S and south of 70°N; this is referred to as the global flux case. The second scenario involved emissions of nPB only from North American landmasses south of 70°N. The third scenario is similar to scenario 2 except that it includes emissions only over the contiguous United States. The fourth scenario assumes emissions over North America, Europe, China, and Japan. The final scenario allowed nPB emissions over India, Southeast Asia, and Indonesia only. Figures 4a–4e show the distribution of emissions assumed for the five cases. A constant land-only nPB surface flux of 2.78×10^{-13} kg m^{-2} s^{-1} was prescribed in each of the cases, or 1.36×10^8 molecules cm^{-2} s^{-1}.

Of interest in these studies are the relative contributions of nPB, ΔBr_y, and BrAc to the change in total stratospheric bromine. For the global emissions case, only about 2% of the nPB emissions released at the ground reach the stratosphere as nPB. Analyzing the relative contributions of nPB, ΔBr_y, and BrAc from the global flux case in the three-dimensional model, it was found that nPB contributes 9.4% to the change in total stratospheric bromine, while ΔBr_y contributes 86.4%, and BrAc contributes 4.2%. This trend is found throughout all emission scenarios although the percentages do change slightly for the different scenarios. For the average of the five different cases, ~12% of the change in total stratospheric bromine is due to nPB directly destroyed in the stratosphere, ~83% is from ΔBr_y transported from the troposphere, while BrAc transported to the stratosphere contributes about 5%. In the two-dimensional model, for the global emissions case and full degradation chemistry, ~14% of the change in total stratospheric bromine is due to nPB directly destroyed in the stratosphere, ~69% is from ΔBr_y transported from the troposphere, 0.4% from other RBr, while BrAc transported to the stratosphere contributes about 16%.

ΔBr_y is the major contributor to the total change in the stratospheric bromine because of the loss processes of the brominated species. The compound nPB reacts with the hydroxyl radical, which is found ubiquitously throughout the troposphere and into the stratosphere, while ΔBr_y is unreactive toward OH. BrAc loss processes include OH reaction, photolysis, and rainout, while the only effective loss mechanism for ΔBr_y is rainout. Water-soluble reservoirs of ΔBr_y are chemically reactive compared to, for example, inorganic chlorine reservoirs, so that rainout of ΔBr_y is slower than would be the case for a Cl_y perturbation due to the larger fraction of ΔBr_y present as less-soluble radical species. Therefore any amount of ΔBr_y which is produced or transported above the cloud deck is available for transport to the stratosphere. From this it is readily understood that nPB itself is not the major contributor to the change in total stratospheric bromine but rather it is ΔBr_y produced from nPB degradation that produces the greatest change in total stratospheric bromine.

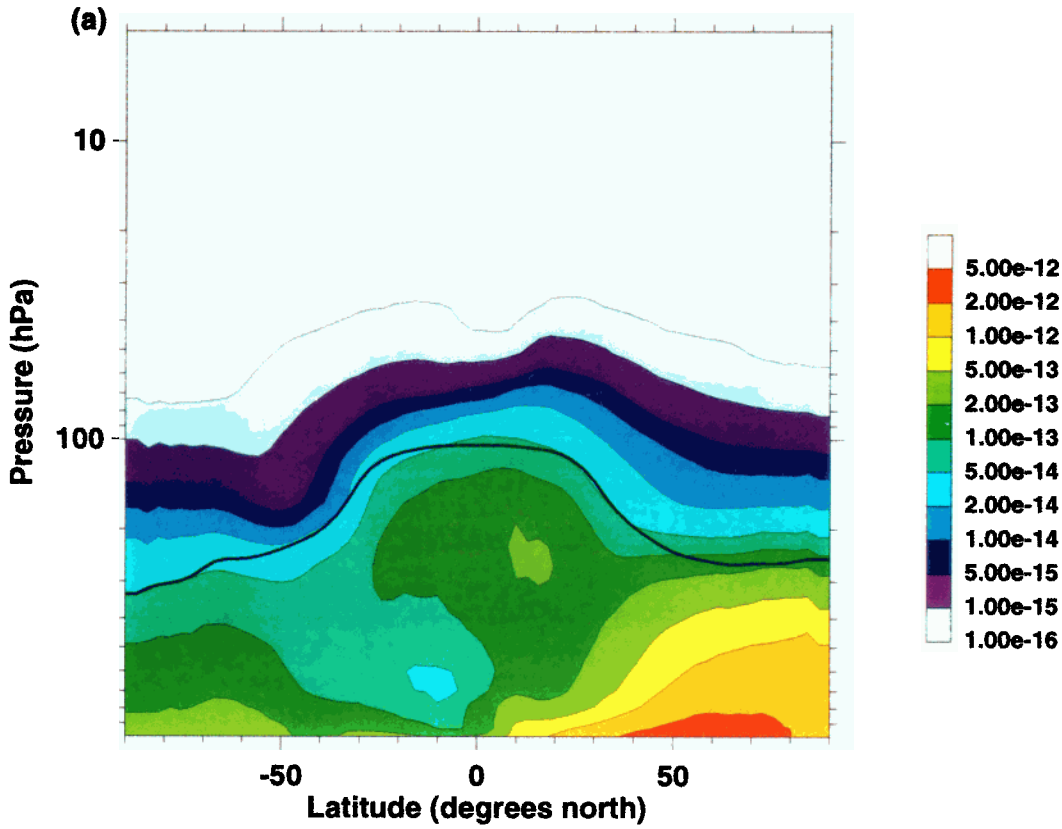
Plate 1 shows the annually and globally averaged mixing ratios as a functions of latitude and altitude for nPB (Plate 1a) and BrAc (Plate 1b) as calculated with the three-dimensional model for the global emissions case. As expected, the mixing ratio of nPB decreases sharply with altitude, with peak concentrations near the ground at midlatitudes in the Northern Hemisphere. Plates 2a and 2b show the corresponding percentages of the tropopause burdens for nPB and for ΔBr_y. The percentage amount of BrAc is typically near 5% of the total (not shown). In many parts of the globe the ΔBr_y is greater than 90%.

We found that we could not adequately compare the stratospheric burden changes in ΔBr_y resulting from the emissions of nPB between the two- and three-dimensional models. The three-dimensional model does not fully represent stratospheric processes and tends to collect too much ΔBr_y in the stratosphere of the model. This is likely due to the upper boundary of the model being located in the middle stratosphere, with the result that the 3-D model is not correctly fully representing stratospheric transport processes. Much of the difference in the evaluation of the bromine reaching the stratosphere as Br_y between the two models may be explained by this effect.

The globally-averaged atmospheric lifetime of nPB determined with the two- and three-dimensional model calculations is about 19–20 days, whereas earlier estimates were 11 to 14 days. As mentioned earlier, this is explainable in terms of the approach used in the global emissions treatment between the earlier and the present studies.

6. Derivation of ODPs

Because a majority of the bromine due to nPB perturbation is expected to be transported to the stratosphere as ΔBr_y and because an additional fraction is likely to be transported as BrAc, the fraction of source gas arriving at the tropopause (β) as used in the "semiempirical" approach to ODP scaling [*So-*



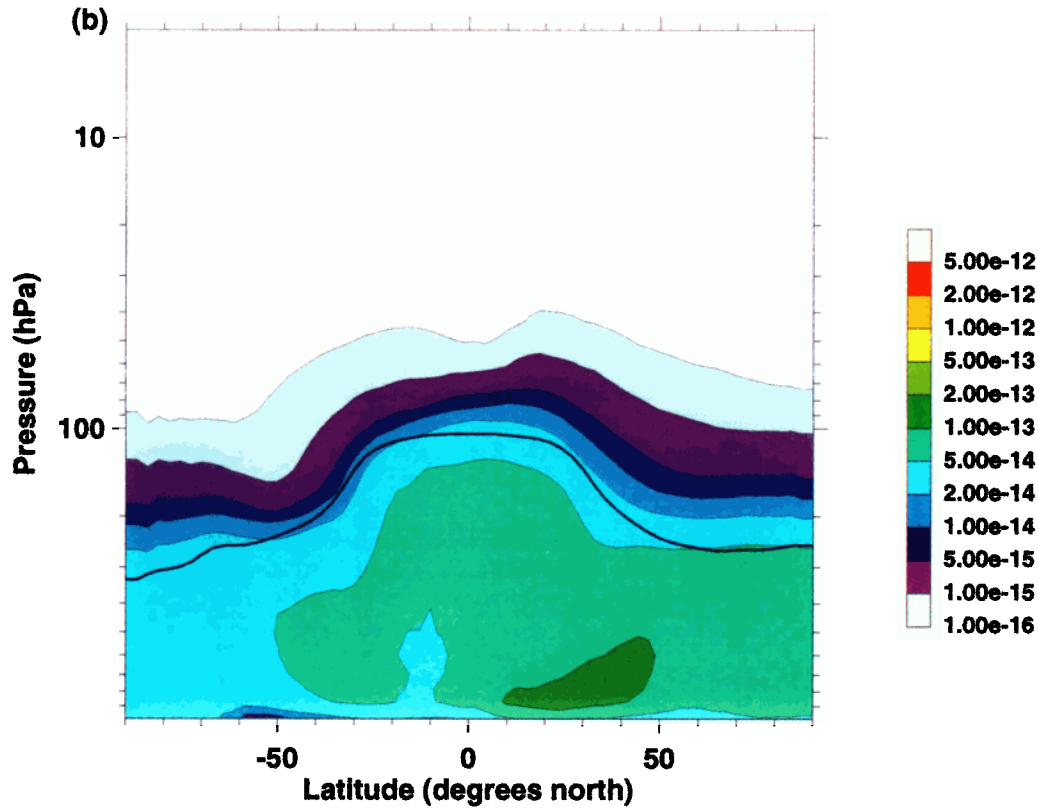
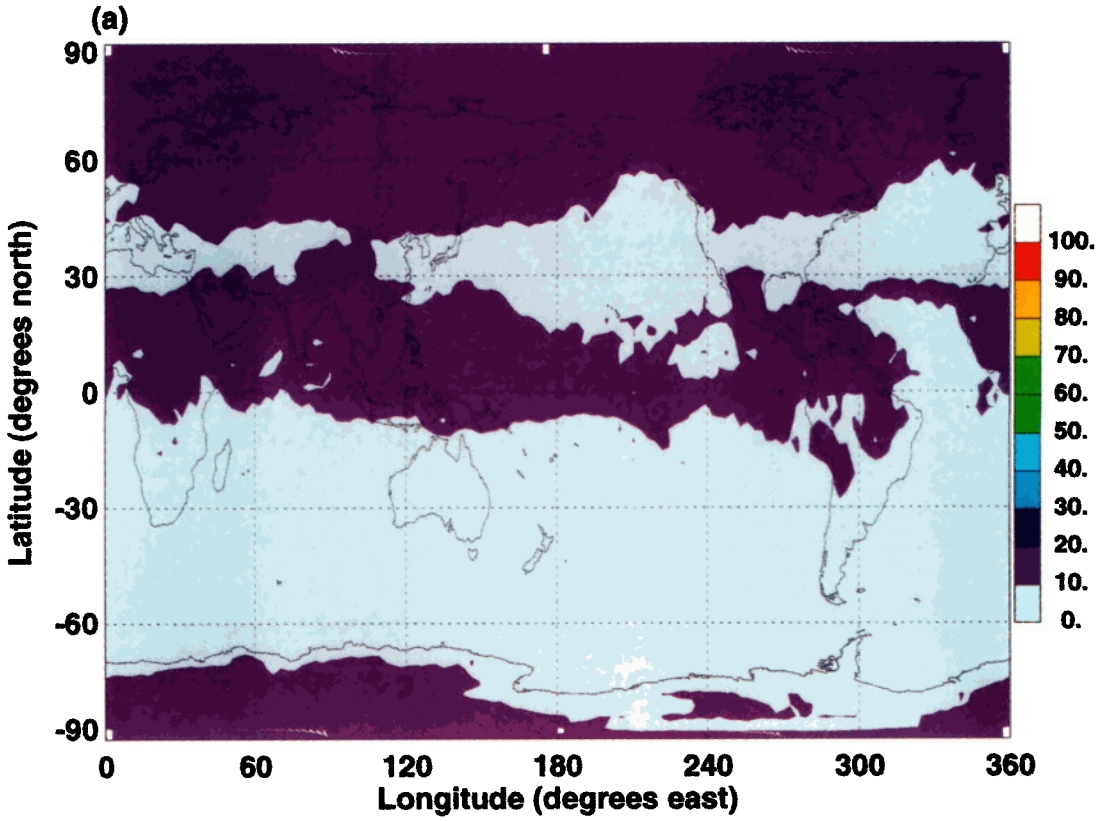


Plate 1. Annually and zonally averaged (a) nPB and (b) BrAc mixing ratios in MOZART2 for the global emissions case. The height of the tropopause is indicated by the solid dark line.



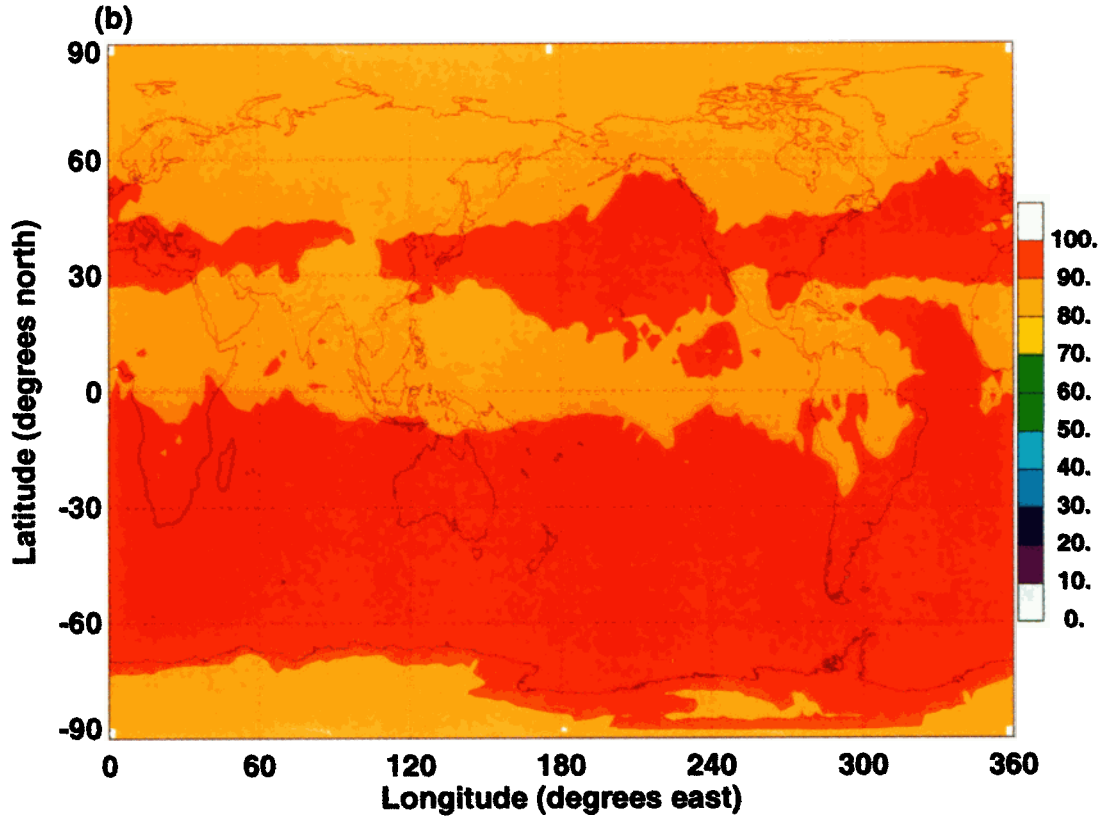


Plate 2. Relative amounts (in percent) of tropopause burdens for (a) nPB and (b) ΔBr_y for the global emissions case in the MOZART2 model.

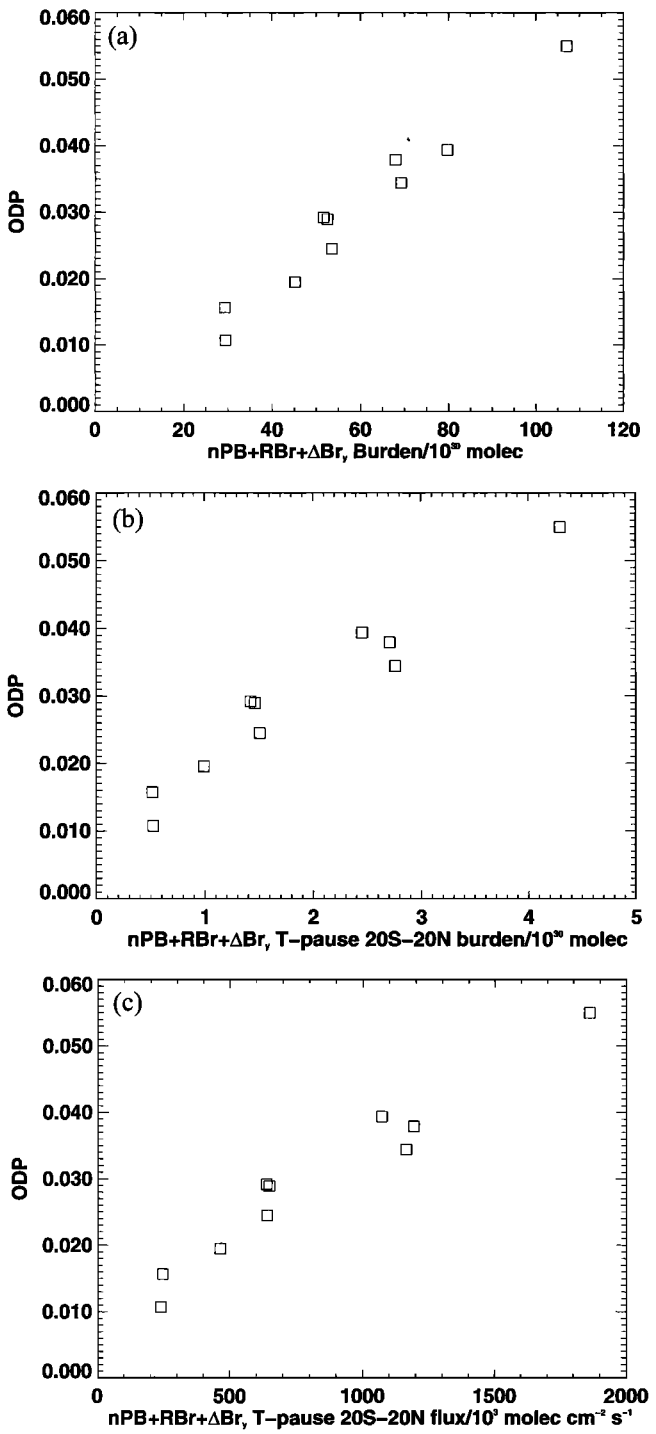


Figure 5. Correlation of n-propyl bromide ozone depletion potentials derived from the two-dimensional model with (a) total stratospheric burden, (b) burden in the layer above tropopause between 20°S and 20°N, and (c) flux across tropopause between 20°S and 20°N.

lomon et al., 1992] should be replaced by the ratio of a quantity summed over the source gas plus its degradation products, both organic and inorganic, to the total source gas emission for the case of nPB. The three parts of Figure 5 illustrate correlations between the two-dimensional model ODPs and three such quantities: the burden above the tropopause in Figure 5a, the burden in the model layer immediately above the tropopause between 20°S and 20°N in Figure 5b, and the flux across the tropopause between 20°S and 20°N (as calculated for Table 4) in Figure 5c. Each of these variables correlates well with the two-dimensional ODP, suggesting that the scaling approach outlined below, to determine the ODPs as a function of location of emissions combining information from the two-dimensional model and the three-dimensional model, MOZART2, is an appropriate approach.

Part of the difficulty in combining results from the 2-D model with those from the 3-D model is sorting out the best scaling factors to modify the ODP values determined from the 2-D model in order to effectively account for the results from the 3-D model for the cases with emissions at varying locations. In this study, two methods were devised for scaling the ODPs derived from the 2-D model. The first method calculates the burden of nPB, ΔBr_y, and BrAc at the tropopause, sums these values, and divides by the emission rate of nPB from the respective model. Dividing by emission rate serves to normalize the values in order to account for the different emission scenarios used, and to account for emission differences between the 2-D and 3-D models. The scaled ODP is then obtained by multiplying the base ODP by the ratio of the 3-D scaling factor to the 2-D scaling factor. The second scaling factor examines the flux of nPB, ΔBr_y, and BrAc across the tropopause. Fluxes yield the actual amount of each species entering the stratosphere, and the sum of the fluxes yields the total bromine flux across the tropopause, due to nPB and its degradation products. As most cross-tropopause transport occurs in the tropics, only average fluxes between 20°N and 20°S were used as scaling factors. A test where we extended the flux average to latitudes between 30°N and 20°S produced unrealistically low values due to inclusion of downward transport associated with the Hadley cell. As in the previous method, the fluxes are normalized by the emission rate. The resulting scaling equations used in this study are as follows:

$$\mathrm{ODP(final)} = \mathrm{ODP}(2 - D)\,\frac{\gamma \text{ or } \delta(3 - D)}{\gamma \text{ or } \delta(2 - D)}, \qquad (1)$$

where

$$\gamma = \frac{\text{tropopause burden (molecules)}}{\text{emission rate (molecules day}^{-1})} \qquad (2)$$

and

$$\delta = \frac{\text{flux across the tropopause from 20°S to 20°N (molecules cm}^{-2}\,\text{s}^{-1})}{\text{emission rate (molecules day}^{-1})}. \qquad (3)$$

We first calculated the ODP for nPB considering the full degradation chemistry discussed in earlier sections in the two-dimensional model with constant evenly distributed global emissions of nPB. As mentioned earlier, this version of the model is also different than previous studies of nPB in the model through changes in the K_{yy} values at the tropopause. The calculated ODP for nPB in the new version of the model is 0.039, somewhat higher than the values we had found previously. The γ scaling factor derived for the two-dimensional model in the global emissions case and full degradation chemistry is 0.661, while the δ value is 3.67×10^{-26}.

For the five cases described earlier we then derived fluxes and burdens for the nPB, the BrAc degradation product, and the ΔBr_y reaching the tropopause. The scaling factors from the

Table 5. Scaling Factors Calculated From MOZART2 From the Five Emission Scenarios[a]

Emission Scenario	Surface Flux, molecules day^{-1}	Species	Tropopause Burden, molecules (90°S–90°N)	Tropopause Flux, molecules cm^{-2} s^{-1} (20°S–20°N)	γ	δ
Global	1.545E + 31[b]	nPB	9.787E + 29	1.572E + 05		
		Br_y	8.967E + 30	2.266E + 05		
		BrAc	4.339E + 29	8.711E + 04		
		total	1.038E + 31	4.710E + 05	0.672	3.049E-26
North America	2.288E + 30	nPB	1.12E + 29	1.493E + 04		
		Br_y	5.62E + 29	1.654E + 04		
		BrAc	4.49E + 28	7.651E + 03		
		total	7.185E + 29	3.913E + 04	0.314	1.710E-26
United States	1.023E + 30	nPB	5.03E + 28	5.480E + 03		
		Br_y	2.63E + 29	7.010E + 03		
		BrAc	2.03E + 28	3.094E + 03		
		total	3.336E + 29	1.558E + 04	0.326	1.523E-26
North America Plus Europe Plus Asia	5.503E + 30	nPB	3.380E + 29	3.742E + 04		
		Br_y	2.100E + 30	4.846E + 04		
		BrAc	1.407E + 29	1.960E + 04		
		total	2.578E + 30	1.055E + 05	0.469	1.917E-26
Indonesia Plus Southeast Asia	9.298E + 29	nPB	1.24E + 29	2.421E + 04		
		Br_y	1 46E + 30	3.717E + 04		
		BrAc	5.64E + 28	1.389E + 04		
		total	1.637E + 30	7.527E + 04	1.760	8.095E-26

[a]Gamma (γ) factors are calculated using equation (2), while delta (δ) factors are calculated using equation (3). The tropopause burden and average flux across the tropopause for individual species is also given. Surface flux values represent the flux of nPB integrated over 1 day.
[b]Read 1.545E + 31 as 1.545×10^{31}.

five runs with the three-dimensional model, including the contribution from individual species, are given in Table 5. The γ scaling factors range from 1.760 to 0.314, over a five-fold range in values. Emissions over North America and the United States yield scalings at the low end of the spectrum, producing γ scaling factors of 0.314 and 0.326, respectively. The global and North America, Europe, and Asia emission scenarios yield γ scalings slightly above the United States and North America emission scenarios. The largest scaling factor occurs when the location of emissions occurs over India, Indonesia, and Southeast Asia. All locations are within tropical latitudes, hence nPB, Br_y, and BrAc are quickly available for transport to the stratosphere through tropical deep convection. For the flux across the tropopause scaling factors (δ), results are similar to γ values. Again, the largest scaling is found from the India, Indonesia, and Asia emission scenario. The only significant difference found in the scenarios is that the United States δ value is slightly smaller than the δ value of the North America scenario, a switch versus the derived γ values.

The resulting ODPs using the scalings described above are shown in Table 6. For all cases the three-dimensional model only accounts for emissions over the given landmasses. The resulting ODP for global emissions has a range of 0.033–0.040. However, the ODP for emissions over North America only is much smaller, 0.018–0.019. Assuming that emissions occur only over the contiguous United States gives similar ODPs to the North America case, 0.016–0.019. Assuming emissions occur evenly over North America, Europe, and Asia (China and Japan) results in an ODP slightly larger, 0.021–0.028. In contrast, emissions in the tropics, from India, Southeast Asia, and Indonesia, result in a much larger ODP, 0.087 to 0.105. This latter result shows the strong effect of the deep convective transport in the tropics in rapidly getting gases to the upper troposphere.

7. Conclusions

As part of the process for better understanding the potential effects of nPB on stratospheric ozone, we have studied the degradation products of nPB and the atmospheric lifetimes of these products. About 19% of the Br atoms are released upon the initial reaction of OH with nPB. Of the other brominated products, only brominated acetone, which accounts for about 71% of the initial nPB degradation, has a sufficiently long enough atmospheric lifetime (~20 days) and large enough production rate to be of concern. The current two-dimensional modeling study suggests that this nPB degradation product

Table 6. Estimated Ozone Depletion Potentials for nPB As a Function of Location of Emissions[a]

Emission Scenario	γ-Scaled ODP	δ-Scaled ODP	ODP Range
Global	0.040	0.033	0.033–0.040
North America	0.019	0.018	0.018–0.019
United States	0.019	0.016	0.016–0.019
North America Plus Europe Plus Asia	0.028	0.021	0.021–0.028
Indonesia Plus Southeast Asia	0.105	0.087	0.087–0.105

[a]Estimates are based on combined results from analyses with the UIUC two-dimensional model and the MOZART2 three-dimensional model. Emissions were evenly distributed over the landmasses based on their representation in the three-dimensional model.

could significantly add bromine to the stratosphere in addition to nPB transported to the stratosphere directly. The three-dimensional modeling studies further substantiate this finding.

The ODPs derived for nPB were found to be strongly dependent on location of the emissions, particularly in terms of emissions in the tropics relative to emissions at higher latitudes. The ODP values for assumed emissions from Indonesia and Southeast Asia are roughly a factor of 5 greater than those for assumed emissions over North America. The ODPs for locations of emissions where nPB is most likely to be used, North America, Europe, and Asia, range from 0.016 to 0.028.

There still remain significant uncertainties in the determination of effects on stratospheric ozone, including the evaluation of Ozone Depletion Potentials, for short-lived gases like n-propyl bromide. In this study, the ODP calculated for global emissions of nPB from the two-dimensional model is 0.039, larger than that determined with earlier versions of the model [*Wuebbles et al.*, 1998, 1999a]. However, the current value reflects the inclusion of the full degradation chemistry and several changes in the model transport processes. By scaling the global results from the two-dimensional model to results from the three-dimensional model for emissions at different locations, we were able to derive ODPs that depend upon emissions location. These ODPs for nPB show a strong dependence to the location of the emissions, especially with respect to latitude.

In the ODP studies we found only small differences between the ODPs derived for the two scaling approaches. Given the remaining questions about the degradation chemistry as discussed earlier as well as uncertainties in the models used, we do not believe there is any real difference between the ODP values of 0.033 and 0.040 found in this study for the global emissions case.

The model studies of short-lived gases like nPB are likely to be quite sensitive to remaining uncertainties in the treatment of various processes in the model. Some of the larger concerns that became obvious as we proceeded through this study are remaining uncertainties about the treatment of convective processes, boundary layer processes, surface deposition, and rainout. The adequacy of the treatment of these processes in MOZART2 is currently being examined as a separate study.

A three-dimensional model with complete representation of stratospheric processes is needed to fully resolve remaining issues. In coordination with NCAR, a new version of the MOZART model, MOZART3, is currently under development that will include tropospheric, stratospheric, and mesospheric processes. However, because of its significant computational requirements, the number of calculations with this model will be quite limited over the next few years.

As discussed earlier, considerable uncertainty in the ozone effects of n-propyl bromide is also associated with the lack of observations of reaction rate constants and products for the degradation chemistry. According to this analysis the most important sources of uncertainty are rate constants specific to where on the n-propyl bromide molecule OH abstracts H, BrAc absorption cross sections and photolysis quantum yields with product identification, and BrAc mass accommodation coefficients and solubility in water (or reaction probability coefficient on water) for rainout. These uncertainties will best be reduced by experimental measurement.

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