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EVALUATION OF OZONE DEPLETION POTENTIALS FOR CHLOROBROMOMETHANE (CH_2ClBr) AND 1-BROMO-PROPANE ($CH_2BrCH_2CH_3$)

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Abstract—Chlorobromomethane (CH_2ClBr) and 1-bromo-propane ($CH_2BrCH_2CH_3$ or simplified as $1-C_3H_7Br$) are being considered for use as solvents and potentially in other applications. As with other chemicals that contain chlorine and/or bromine, it is important to determine the potential environmental effect from use and emissions of such compounds, including effects on stratospheric ozone. In this paper, the Ozone Depletion Potentials (ODPs), an important measure of the potential effects on ozone, are evaluated for these two compounds using our two-dimensional chemical-transport model of the troposphere and stratosphere. This is the first time these compounds have, to our knowledge, been evaluated with atmospheric models. Our model results show that the main removal process (*ca.* 99%) in the atmosphere for these compounds is the reaction with OH radicals. Photolysis has only a minor ($\leqslant 1\%$) effect on the atmospheric lifetimes of either compound. The atmospheric lifetimes of CH_2ClBr and $1-C_3H_7Br$ due to atmospheric reactions are evaluated to be 0.40 yr (146 d) and 0.03 y (11 d), respectively. However, oceanic losses are likely to be important for CH_2ClBr. Because of limited data on solubility and degradation in sea water, the lifetime for ocean loss currently has a range of 0.43–0.65 yr. This results in a total lifetime for CH_2ClBr of 0.21–0.25 yr. An ocean sink for $1-C_3H_7Br$ is likely to have an insignificant effect on its atmospheric lifetime or ODP. The ODP for $1-C_3H_7Br$ is evaluated to be 0.006, while the ODP for CH_2ClBr including the effects of the ocean sink is 0.11–0.13. There are additional uncertainties in these values due to ambiguities in measured reaction rates and in the model treatment of atmospheric processes. © 1997 Published by Elsevier Science Ltd

INTRODUCTION

International regulatory actions (UNEP, 1987) have led to the phase out of production of chlorofluorocarbons (CFCs), halons, and several other halocarbons. This decision has prompted significant interest in the development of possible replacements for CFCs and other industrially produced compounds. As part of the development of such compounds, it is necessary to consider the potential environmental effects from their use and possible emissions into the atmosphere. Their potential effects on stratospheric ozone need to be evaluated. For these compounds to be environmentally acceptable, it is necessary to ensure that their impact on the environment is small. The concept of Ozone Depletion Potentials (ODPs), developed by Wuebbles (1981), has become a standard means for evaluating the effects of a compound relative to concerns about other chemicals on stratospheric ozone (Wuebbles, 1983; 1995; WMO, 1991, 1995; Albritton *et al.*, 1995; Solomon *et al.*, 1995). As an example, this concept is an integral part of national and international policy considerations to protect ozone, including the international Montreal Protocol on Substances That Deplete the Ozone Layer and its Amendments and the U.S. Clean Air Act.

The ODP for a compound is defined as the steady-state calculated ozone depletion for each unit mass of a gas emitted into the atmosphere taken in ratio to the steady-state calculated ozone depletion per unit mass emission of CFC-11. As such, ODPs are used to examine the relative potential effects on ozone from a variety of chemicals, particularly halogenated compounds containing chlorine, bromine or iodine (see, e.g., WMO, 1995; Solomon *et al.*, 1995; Wuebbles, 1995). On an equal mass basis, the ODP is a measure of the cumulative effect on ozone for a given compound compared to the cumulative effect calculated for CFC-11.

Chlorobromomethane (CH_2ClBr) and 1-bromopropane ($CH_2BrCH_2CH_3$ or simplified here as $1-C_3H_7Br$) are two of the many compounds being considered as replacements for CFCs and halons for a number of uses, including as solvents, refrigerants, plastic foam blowing agents or as fire suppressants. Both of these gases are currently being considered as solvents. Both also contain bromine which can react catalytically with ozone in the Earth's atmosphere (WMO, 1995). Although their current atmospheric concentrations are negligibly small, these compounds can influence the reactive bromine budget in the atmosphere, particularly in the lower stratosphere where bromine is most effective at destroying ozone. Their efficiency in affecting ozone will depend on the amounts reaching the stratosphere. In this study, we evaluate the atmospheric lifetimes and ODPs of CH_2ClBr and $1-C_3H_7Br$. As far as we are aware, the atmospheric lifetimes and ODPs for these compounds have not previously been evaluated with chemical-transport models of the global atmosphere and published in the scientific literature.

MODEL DESCRIPTION AND APPLICATION

We have calculated the atmospheric lifetimes and ODPs for CH_2ClBr and $1-C_3H_7Br$ using our two-dimensional photochemical transport model of the global atmosphere (e.g. Kinnison *et al.*, 1994; Wuebbles *et al.*, 1991, 1996). This model has been used extensively in the past international ozone assessments to determine ODPs and other effects on ozone from CFCs and other halocarbons (e.g. WMO, 1991, 1995). The model's grid is 5° in latitude from pole to pole and about 1.5 km in altitude from the surface to 85 km. Transport of species in the model is self-consistently calculated using the predicted model ozone and seasonally varying climatological temperatures. The photochemical mechanism typically represents the chemical and physical interactions of about 50 chemical species and stratospheric aerosols and accounts for about 150 chemical and photochemical reactions in the atmosphere. The kinetic and spectral parameters are taken primarily from the NASA JPL recommendations (DeMore *et al.*, 1994). Effects of heterogeneous chemistry on sulfate aerosols and polar stratospheric clouds are included in the model. Rainout in the troposphere is included for water soluble species including those involving chlorine and bromine such as HCl and HBr.

A significant change in the rate for the heterogeneous reaction involving bromine nitrate hydrolysis ($BrONO_2 + H_2O$) on sulfate aerosols has been included based on Hanson and Ravishankara (1995); in this study the sticking coefficient γ is assumed to be 0.6 based on private communication with Ravishankara (note that more recent work by Hanson and Ravishankara suggests that a composition dependence should also be included, but it should not significantly affect the results presented here).

The new chemistry added for this study of CH_2ClBr and $1-C_3H_7Br$ is shown in Table 1. The loss rates for CH_2ClBr and $1-C_3H_7Br$ are determined by reaction with hydroxyl (OH) and through photolysis. For $1-C_3H_7Br$, we also considered the loss rate due to reaction with chlorine (Cl) atoms. The rate constants for the reactions of CH_2ClBr with OH and of $1-C_3H_7Br$ with OH and Cl are obtained from laboratory measurements of Orkin *et al.* (1997) and Donaghy *et al.* (1993), respectively. The photolysis absorption cross section data for CH_2ClBr is taken from Orkin *et al.* (1997). However, we are unable to find cross-section data for $1-C_3H_7Br$ in the literature. In this study, the photolysis of $1-C_3H_7Br$ is determined based on the absorption cross-section data of CH_3Br, which is the closest chemical analog for which we have cross sections. The absorption cross-section data for CH_3Br is taken from DeMore *et al.* (1994).

For the ODP calculations, the emission rates for CFC-11, and those for CH_2ClBr and $1-C_3H_7Br$ are chosen to give a modeled ozone depletion of about 1%, thus giving a response at a level well above the numerical noise of the model while also attempting to avoid significant non-linearities in the response of ozone expected for larger perturbations. For each compound, three runs are needed to define a model-calculated ODP: a reference unperturbed ambient atmosphere; a reference perturbation; and a perturbation

Table 1. Chemical reactions and associated rate constants added to the two-dimensional chemical-transport model for this study

Chemical reaction	Arrhenius expressions for rate constants (cm^3 $molecule^{-1}$ s^{-1})	Source
Thermal reactions		
$CH_2ClBr + OH = Br + Cl + H_2O$	$(3.1 \pm 0.7) \times 10^{-12} exp[-985 \pm 67)/T]$	Orkin *et al.* (1997)
$1-C_3H_7Br + OH = Br + H_2O + CH_3O_2$	$(6.3 \pm 1.6) \times 10^{-12} exp[-500 \pm 125)/T]$	Donaghy *et al.* (1993)*
$1-C_3H_7Br + Cl = HCl + Br + CH_3O_2$	$(61 \pm 18) \times 10^{-12}$	Donaghy *et al.* (1993)
Photolysis reactions		
$CH_2ClBr + h\nu = Br + Cl$		Orkin *et al.* (1997)
$1-C_3H_7Br + h\nu = Br + CH_3O_2$		See text

*Activation energy based on consideration of similar compounds.

of compound of interest. The model is first run to steady-state with current surface mole fractions specified for Cl- and Br-containing source gases, which produces the current levels of equivalent stratospheric chlorine (*ca.* 3 ppbv). Since the current atmospheric abundance of CH_2ClBr and $1-C_3H_7Br$ are expected to be quite small, their global distributions in the background (*ca.* 1990) atmosphere are assumed to be zero. Second, the surface abundance of CFC-11 is increased from 270.0 pptv to 370.0 pptv and the model is run to steady-state to establish the sensitivity of ozone to a CFC-11 perturbation. The 100 pptv perturbation in CFC-11 (equivalent to a 0.04 Tg emission rate) produces roughly a 1% total column ozone change. Third, the surface abundances of CH_2ClBr and $1-C_3H_7Br$ are perturbed one at a time and the model is run to steady-state to establish the sensitivity of ozone to CH_2ClBr and $1-C_3H_7Br$ perturbations. In order to produce about 1% ozone changes, the perturbations in surface concentrations of 4.93 pptv (equivalent to 0.16 Tg per year as surface flux) for CH_2ClBr and 21.4 pptv (equivalent to 4.24 Tg per year flux) for $1-C_3H_7Br$ were required. Calculations were done using both surface concentration and flux boundary conditions, but did not indicate significant differences in the results.

Figures 1a–c show the model-estimated total column ozone changes produced by CFC-11, CH_2ClBr and $1-C_3H_7Br$ perturbations. Although the total ozone depletion in all three cases is the same, the distribution with latitude and season are different, following the different photolysis reaction rate constants and photolysis absorption data for CFC-11, CH_2ClBr and $1-C_3H_7Br$. The largest effects are seen in the polar spring where polar stratospheric cloud processes increase the efficiency of the Cl- and Br-driven catalytic ozone loss. Figure 2 shows the altitude distribution at 45 N of the change in ozone for all three cases. As expected, because of the relative effects with altitude for chlorine and bromine to destroy ozone, there is a significant difference in the ozone perturbation in altitude for the three cases.

DERIVED ATMOSPHERIC LIFETIMES AND ODPS

Our model-estimated global atmospheric lifetime of CFC-11 is 56.6 yr, which is somewhat higher than the recent IPCC assessment of 50 yr (IPCC, 1996). In determining ODPs the values are scaled to account for this lifetime difference in order to put the derived ODPs on the same scaling used in the WMO (1995) assessment. The model-estimated atmospheric lifetimes for CH_2ClBr and $1-C_3H_7Br$ due to atmospheric chemical loss are 0.40 yr (146 d) and 0.03 yr (11 d), respectively. In deriving these atmospheric lifetimes, the model-derived lifetimes have been scaled based on the observation-based lifetime of 5.9 yr for methyl chloroform (CH_3CCl_3) due to reaction with tropospheric OH (WMO, 1995; Prinn *et al.*, 1995).

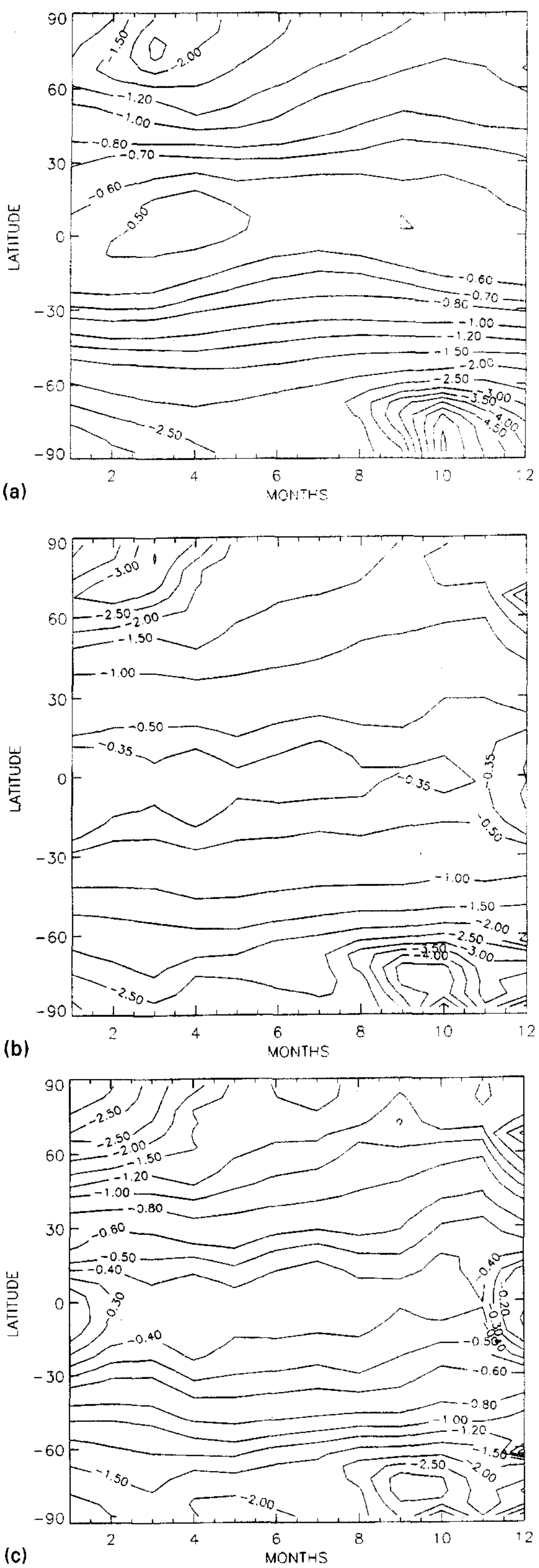

Fig. 1. Change in total column ozone (in %) produced by assumed perturbations to surface emissions of (a) CFC-11, (b) CH_2ClBr, and (c) $1-C_3H_7Br$ as a function of season and latitude. The distribution averages to a 1% global ozone decrease.

This scaling is also done in the derivation of lifetimes and ODPs in the international assessments (WMO, 1995).

The main removal process for CH_2ClBr and $1-C_3H_7Br$ is the reaction with OH radicals. The reaction of CH_2ClBr with OH represents *ca.* 99% of the globally averaged loss of this gas, while the OH-, and Cl-driven losses of $1-C_3H_7Br$ account for *ca.* 98% and *ca.* 2%, respectively. The atmospheric photolysis has only a minor effect ($\leq 1\%$) on the atmospheric lifetimes of either compound. As discussed below, loss to the ocean also needs to be considered for these compounds in determining their total atmospheric lifetimes.

The ODPs for CH_2ClBr and $1-C_3H_7Br$ calculated from our two-dimensional chemical-radiative transport model due to consideration of atmospheric loss only are presented in Table 2. As mentioned above, in order to account for uncertainties in model-derived atmospheric lifetimes, the model-estimated ODPs are normalized to a CFC-11 lifetime of 50 yr, and to an OH-driven methyl chloroform (CH_3CCl_3) lifetime of 5.9 yr, as determined from available atmospheric measurements (WMO, 1995; Prinn *et al.*, 1995). The CFC-11 and CH_3CCl_3 scaling accounts for uncertainties associated with determining the Cl and OH distributions in the model. The normalized ODPs derived for CH_2ClBr and $1-C_3H_7Br$ when we consider atmospheric loss only are 0.21 and 0.0064, respectively (see Table 2). These ODPs assume reactions in the atmosphere are the only important processes in the removal of these compounds after their emission. As discussed below, removal in the ocean is also important for determining the ODP of CH_2ClBr.

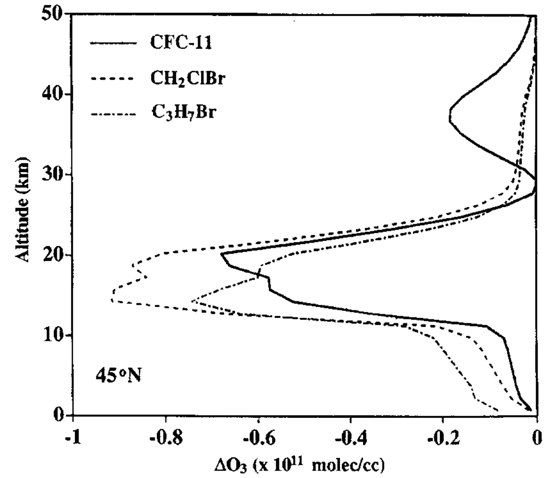

Fig. 2. Absolute change in ozone at 45 N in density units (molecules/cm^3) for the assumed perturbations to surface emissions of CFC-11, CH_2ClBr, and $1-C_3H_7Br$.

To provide a sense of confidence in the model results and for comparison with earlier analyses of ODPs, we also derived the atmospheric lifetime and ODP for methyl bromide, CH_3Br. The atmospheric lifetime derived for CH_3Br due to its reaction with OH is 1.85 yr. In the 1994 international assessment on ozone (WMO, 1995), the partial lifetime for methyl bromide associated with ocean loss was estimated to be 3.7 yr with large error bars based on Butler (1994). This value was used in determining the overall lifetime and ODP for CH_3Br in that assessment. Using this loss rate reduces the total lifetime of CH_3Br to 1.23 yr, in quite good agreement with the estimated lifetime in WMO (1995). With this lifetime, we derive an ODP for CH_3Br of 0.65, in excellent agreement with the value of 0.64 evaluated by modeling studies in WMO (1995) which had an overall uncertainty range of 0.52–0.76.

Shorter *et al.* (1995) suggest that a soil sink for CH_3Br is also likely to be important. Including this loss with a partial lifetime of 3.4 yr, as suggested in their paper, reduces the total lifetime to 0.90 yr and reduces the ODP to 0.48 yr.

Table 2. Model-estimated atmospheric lifetimes (τ) and ozone depletion potentials (ODPs) for CH_3Br, CH_2ClBr and $1-C_3H_7Br$

	Atmospheric lifetime τ (yr)					
Gas	τ^{a}_{OH}	τ_{Cl}	$\tau_{photolysis}$	τ_{ocean}	τ^{f}_{total}	ODP
CH_3Br	1.85			3.7[b]	1.23	0.65
				1.9[c]	0.92	0.49
				w/soil	0.73[g]	0.38
CH_2ClBr	0.40		63.3	0	0.40	0.21
				0.43–0.65[d]	0.21–0.25	0.11–0.13
$1-C_3H_7Br$	0.031	1.761	32.5	0	0.030	0.0064
				0.5–1.9[e]	0.028–0.30	~0.006

[a] Normalized to a OH-driven CH_3CCl_3 lifetime of 5.9 yr.
[b] Based on Butler (1994).
[c] Based on Yvon-Lewis and Butler (1997).
[d] Based on evaluation of ocean sink (J. Butler, private communication, 1997).
[e] Estimated ocean sink.
[f] Total lifetime based on all losses; normalized to CFC-11 lifetime of 50 yr, and OH-driven CH_3CCl_3 lifetime of 5.9 yr.
[g] Overall lifetime including effect of soil sink for CH_3Br.

More recently, studies of the ocean loss found first a partial lifetime of 2.7 yr in an improved analysis by Yvon and Butler (1996) and then 1.8–1.9 yr by better accounting for biological degradation (Yvon-Lewis and Butler, 1997). The uncertainty in this partial lifetime has now been reduced to 1.1–3.9 yr. Using a partial lifetime of 1.85 yr for the ocean loss in combination with our loss due to OH and the loss to soils reduces the overall lifetime to 0.73 yr. As shown in Table 2, the ODP for CH_3Br is now reduced to 0.38.

EFFECTS OF OCEAN LOSS ON CH_2ClBr AND $1-C_3H_7Br$

In coordination with J. Butler (private communication, 1997), we have estimated a loss rate for CH_2ClBr into the ocean based on the limited solubility data available for CH_2ClBr and estimates of the degradation of CH_2ClBr in the ocean. The only data currently available for solubility is from Orkin *et al.* (1997) where they measured the solubility of CH_2ClBr in distilled water at room temperature. The degradation of CH_2ClBr in the ocean should be somewhere between the degradation loss of CH_3Br and total removal. Using the approach outlined in their previous analyses (Butler, 1994; Yvon and Butler, 1996, Yvon-Lewis and Butler, 1997), we determined a partial lifetime due to ocean loss for CH_2ClBr of 0.43–0.64 yr.

As seen in Table 2, using the ocean loss rate in combination with our derived loss due to reaction with OH gives an overall lifetime for CH_2ClBr of 0.21–0.25 yr. Correspondingly, including the ocean loss gives an ODP for CH_2ClBr of 0.11–0.13.

Orkin *et al.* (1997) estimated the atmospheric lifetime and ODPs for CH_2ClBr based on its reaction with OH and an assumed oceanic removal. They estimated the OH-driven lifetime by a simple scaling procedure of Prather and Spivakovsky (1990) using the reaction rate with OH derived from their laboratory studies. The partial lifetime due to ocean loss was based on their observations of the solubility and by assuming that any dissolution of CH_2ClBr in the ocean leads to chemical degradation (Butler, 1994; WMO, 1995). Their OH-driven atmospheric lifetime (*ca.* 0.43 yr) is similar to our model-estimated OH-driven lifetime. Including the ocean loss (0.42 yr) reduced their overall lifetime to 0.21 yr, again in good agreement with our results. However, their roughly estimated ODP of 0.14 for atmospheric chemical loss is significantly lower than determined with our model (0.21). However, the approach used to estimate the ODP in their analysis makes several assumptions that do not hold with short-lived chemicals (those with atmospheric lifetimes significantly less than a year). In particular, the equation used in their derivation assumes that the compound is well mixed in the troposphere, with little gradient between the ground and tropopause; as will be discussed later, this does not hold for CH_2ClBr.

As far as we aware, there is no data available on the solubility and degradation of $1-C_3H_7Br$ in sea water. If we assume that its loss to the ocean should be between that for CH_2ClBr and CH_3Br, i.e, assuming a partial lifetime of 0.5–1.9 yr, then there is only a very minor effect on the overall lifetime and on the derived ODP for $1-C_3H_7Br$ (see Table 2).

It is important to recognize that the absolute magnitude of the oceanic sink for CH_2ClBr is not well defined at present, mainly because of the remaining uncertainties in its solubility and degradation rate. Measurements are needed of the solubility and degradation in sea water over a temperature range of 0–30°C.

UNCERTAINTIES IN DERIVED ODPs

With few exceptions, the CFCs, halons, and replacement compounds examined previously (e.g. WMO, 1995) have had atmospheric lifetimes sufficently long that they are well mixed in the troposphere. That is not the case for these two compounds. The ODP depends directly on the amount of a compound reaching the stratosphere. For these two compounds only a small percentage of the emissions at the ground reach the stratosphere ($\sim 2\%$ for CH_2ClBr). Thus, uncertainties in the treatment of tropospheric chemistry and transport processes in the model are amplified relative to many of the other compounds examined previously. Although scaling relative to the "observed" atmospheric lifetime for CH_3CCl_3 is used to compensate for uncertainties relative to the concentrations of OH, this is not sufficient to account for uncertainties in other processes, particularly in the treatments of tropospheric transport and tropospheric-stratospheric exchange.

A well evaluated three-dimensional model would be much more appropriate for determining the potential effects on stratospheric ozone from such short-lived chemicals, but currently these models are still too computationally intensive to be used extensively for such studies. However, we can examine some of the uncertainties associated with evaluating the ODPs for these compounds.

One of the key questions for short-lived compounds is the effect on ODP resulting from where the emissions occur. In the basic calculations, as in the WMO assessment studies, fixed concentration or emissions are assumed to be the same at all latitudes. However, for these compounds, emissions should primarily be at midlatitudes in the northern hemisphere. Several additional calculations were done for CH_2ClBr to test the effect of this (similar calculations were not done for $1-C_3H_7Br$ because its ODP was already extremely small). We evaluated the ODP for CH_2ClBr assuming the emissions were confined to either the northern hemisphere or to 30–60° North in addition to the global emissions case. In each case, the ODP determined was essentially the same. Given that most of the emissions should reach the stratosphere through the Hadley circulation in the tropics, this result was somewhat surprising. However, the amount reaching the stratosphere was almost the same for each case, indicating that the same effect on ozone would be expected.

Another uncertainty for short-lived gases is associated with the actual amount reaching the stratosphere. Schauffler *et al.* (1993) measured the concentrations of a number of halocarbons, including several that are short-lived ($CHCl_3$, CH_2Cl_2, and CH_2Br_2), at the tropical tropopause. For these measurements, made at 23.8°N to 25.3°N, they determined a ratio between the surface values and those measured at the tropical tropopause of 0.4–0.5. In our model calculations, at these latitudes, we determined a ratio of 0.41 for CH_2ClBr, in good agreement with these observations. Nonetheless, there remains uncertainty about the transport of these short-lived compounds from the ground to the lower stratosphere where the bromine and chlorine has its largest effect on ozone.

Although difficult to quantify, uncertainties in the treatment of model chemistry and transport should add at least $\pm$ 25% uncertainty to the model-derived ODPs. Given that current models still underestimate the observed ozone change in the lower stratosphere over recent decades (WMO, 1995), any changes in the chlorine or bromine chemistry affecting the explanation of the ozone trend would also tend to affect the derived ODPs.

CONCLUSIONS

In this paper we have evaluated the atmospheric lifetimes and ODPs for CH_2ClBr and $1 - C_3H_7Br$ using our two-dimensional photochemical transport model. We have also reevaluated the atmospheric lifetime and ODP for CH_3Br. CH_2ClBr and $1 - C_3H_7Br$ are currently being considered for use as solvents. The dominant removal process in the atmosphere for these compounds is via reactions with OH radicals, thus much of these compounds react with OH radicals in the troposphere (and are thus removed) before transportation to the stratosphere where the bromine (and chlorine in the case of CH_2ClBr) in these compounds can effectively destroy ozone.

The evaluated lifetime and ODP (1.23 yr and 0.65, respectively) for CH_3Br including oceanic loss at the rate used in the international assessments (WMO, 1995) gives quite similar results to those published. However, including more recent information on the ocean loss and a soil sink for CH_3Br reduces the overall lifetime to 0.73 yr and the ODP to 0.38.

The estimated atmospheric lifetimes and ODP for CH_2ClBr without oceanic removal effects are 0.40 yr and 0.21, respectively. Including oceanic removal effects for CH_2ClBr at a partial lifetime of 0.43–0.65 yr reduced the estimated atmospheric lifetimes and ODP of CH_2ClBr to 0.21–0.25 yr and 0.11–0.13. However, the absolute amount of CH_2ClBr that is absorbed by ocean is still debatable because no systematic studies of the total degradation rate of CH_2ClBr in sea water have been conducted.

The estimated atmospheric lifetime and ODP for $1 - C_3H_7Br$ are 0.03 yr (11 d) and 0.006. Inclusion of an estimated ocean sink has no significant effect on the lifetime and ODP for $1 - C_3H_7Br$.

The estimated ODPs of CH_2ClBr and $1 - C_3H_7Br$ are much smaller than for CFCs or Halons. The ODP for $1 - C_3H_7Br$ is the smallest of any species containing bromine that have been evaluated so far. There remain significant uncertainties in evaluating the atmospheric lifetimes and ODPs for such short-lived gases, particularly relating to uncertainties in the model treatment of tropospheric processes. Even with the scalings used to attempt to account for some of the uncertainties, the ODPs derived here are not known to be better than $\pm$ 25%.

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