Timescales in atmospheric chemistry: 
\( \text{CH}_3\text{Br}, \) the ocean, and ozone depletion potentials

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Abstract. Methyl bromide (\( \text{CH}_3\text{Br} \)) supplies about half of the chemically active bromine (\( \text{Br}_x \)) in the stratosphere. Efforts to control \( \text{Br}_x \)-catalyzed ozone depletion by phasing out, for example, agricultural use of \( \text{CH}_3\text{Br} \) may be thwarted by a lack of understanding of how the varied biogeochemical processes interact as a coupled system: in addition to the chemical industry, large natural sources come from the ocean, and losses occur in the atmosphere, ocean, and soils. A simplified one-dimensional stratosphere-troposphere-ocean model for \{\text{CH}_3\text{Br}, \text{Br}_x \} that fits current understanding of sources and sinks is analyzed in terms of natural modes. Surface and ocean sources have effectively different steady state lifetimes (1.0 and 0.5 years, respectively), but the natural-mode decay times of the system (1.8 years for \( \text{CH}_3\text{Br} \) and 4.5 years for stratospheric \( \text{Br}_x \)) do not depend on the location of sources. The cumulative ozone depletion resulting from a single atmospheric release of \( \text{CH}_3\text{Br} \) integrates over the consequent slow rise and fall of \( \text{Br}_x \) in the lower stratosphere. Thus, in spite of the 1-year lifetime of \( \text{CH}_3\text{Br} \), only half of the anticipated ozone recovery occurs in the first 7 years.

1. Introduction

Protection of the stratospheric ozone layer, our shield against damaging solar ultraviolet radiation, has been largely achieved through international protocol [Montreal, 1987]. The idea that human activities could severely deplete the ozone on a global scale was first proposed [Crutzen, 1970; Johnston, 1971; Molina and Rowland, 1974] and then established in the last 3 decades through the individual research of many scientists and the international scientific assessments [World Meteorological Organization (WMO), 1986, 1992, 1995]. It was recognized by the award of the 1995 Nobel Prize in Chemistry to Crutzen, Molina, and Rowland. Many trace gases measured in the stratosphere are changing as a result of human activity and are identified with potential ozone depletion: odd-nitrogen [Johnston, 1971; McElroy et al., 1977]; chlorine [Molina and Rowland, 1974; Stolarski and Cicerone, 1974]; methane [Ehhalt, 1974]; and bromine [Wofsy et al., 1975]. Of all, bromine is the most potent on a molecule-per-molecule basis.

The primary source gases identified with transporting bromine into the stratosphere have been well measured [Schauffler et al., 1993]. Their decay in the stratosphere is consistent with the release of chemically active bromine (\( \text{Br}_x \)), in particular \( \text{BrO} \), the primary bromine radical in the catalytic destruction of ozone [Brune et al., 1989; Carroll et al., 1989; Toohey et al., 1990]. Currently identified sources of stratospheric bromine are methyl bromide (\( \text{CH}_3\text{Br} \), 10 parts per trillion (ppt)), halon-1211 (\( \text{CF}_2\text{ClBr} \), 3.4 ppt), halon-1301 (\( \text{CF}_3\text{Br} \), 2.3 ppt), and halon-2402 (\( \text{CF}_3\text{BrCF}_2\text{Br} \), 0.7 ppt) [WMO, 1995; Schauffler et al., 1993; Montzka et al., 1996]. Production of halons is already phased out under the amended Montreal Protocol, so attention focuses on \( \text{CH}_3\text{Br} \) as a potential quick fix [WMO, 1995] to ameliorate the peak ozone depletion expected over the next decade [Jachman et al., 1996; Prather et al., 1996]. This paper examines our ability to control the abundance of methyl bromide and the consequent ozone depletion.

Atmospheric \( \text{CH}_3\text{Br} \) comes in part from agricultural and other industrial uses of this compound [McCulloch, 1992; Duaifia, 1995], but its abundance appears to be buffered by a large oceanic biological source and an oceanic chemical sink [see Butler, 1994; Elliott and Rowland, 1993; Lobert et al., 1995; Yvon and Butler, 1996; Anbar et al., 1996]. Current assessments have assumed a simple e-folding model for the impact of anthropogenic \( \text{CH}_3\text{Br} \) emissions, using a global-mean atmospheric lifetime of 1.3 years that includes atmospheric and oceanic losses, but not the recently discovered soil sink [Shorter et al., 1995]. It is shown here that the simple exponential decay, adequate for long-lived gases like halon 1301, does not describe the atmospheric response of \( \text{CH}_3\text{Br} \), nor the rate of ozone recovery.

This paper presents a one-dimensional (1-D) time-dependent stratosphere-troposphere-ocean model for \( \text{CH}_3\text{Br} \) and \( \text{Br}_x \) in section 2 and uses natural modes [Prather, 1994, 1996] to study the temporal behavior of this system for changes in \( \text{CH}_3\text{Br} \) emissions. The spatial patterns and e-fold timescales of the modes are derived in section 3. Several constants for geochemical systems can be defined with units of time: global-mean lifetime, which is based on budgets (total content divided by the sum of all loss rates); mean lifetime against loss.
in one reservoir (total-content / reservoir-loss); turnover time of an individual reservoir (inverse of loss frequency [Bolin and Rodhe, 1973]); and the inverse eigenvalues of the linearized differential equations [Prather, 1994]. It is these latter constants which are the true timescales describing how the atmosphere responds to anthropogenic CH<sub>3</sub>Br emissions. Such response is not affected by the magnitude of the oceanic source. The removal of stratospheric Br<sub>y</sub> (and hence the recovery of ozone) proceeds at a much slower rate, independent of the CH<sub>3</sub>Br timescales. Section 4 compares the ozone depletion potentials (ODPs) derived from assessments with those from the true time-dependent evolution of CH<sub>3</sub>Br and Br<sub>y</sub>. Section 5 compares natural modes and their timescales with different steady state solutions and considers what other chemical systems may yield unexpected results.

### 2. A 1-D Chemical-Diffusion Model

The \{CH<sub>3</sub>Br, Br<sub>y</sub>\}-system can be represented by a one-dimensional diffusive atmosphere [e.g., Logan et al., 1978] with additional exchange between an ocean layer and the lowest atmospheric layer. CH<sub>3</sub>Br is destroyed primarily by OH reaction in the troposphere, by photolysis in the stratosphere, by reaction in soils, and by nucleophilic displacement and hydrolysis in the ocean. The bromine species formed after atmospheric destruction of CH<sub>3</sub>Br (i.e., Br<sub>x</sub>, Br<sub>y</sub>, HBBr, HOBr, BrONO<sub>2</sub>) are designated collectively as Br<sub>x</sub>. (Ozone depletion is assumed to be proportional to stratospheric Br<sub>x</sub>, and this paper considers only the Br<sub>y</sub> from CH<sub>3</sub>Br.) Production of Br<sub>y</sub> matches loss of CH<sub>3</sub>Br and Br<sub>x</sub> is conserved in the stratosphere but washed out in the troposphere. The continuity equations (1) for the densities of CH<sub>3</sub>Br and Br<sub>y</sub> can be written in terms of the emissions P and loss frequencies L for each layer, and the divergence of the diffusive flux \( \nabla \Phi \). This model, defined in Table 1, is taken as linear in that CH<sub>3</sub>Br does not perturb OH concentrations or oceanic hydrolysis rates. (The possible coupling of Br<sub>y</sub> with ozone depletion and enhanced UV is not considered.)

\[
\begin{align*}
\text{d}[\text{CH}_3\text{Br}] / \text{dt} &= -\nabla \Phi_{\text{CH}_3\text{Br}} + P - L \cdot [\text{CH}_3\text{Br}] \\
\text{d}[\text{Br}_y] / \text{dt} &= -\nabla \Phi_{\text{Br}_y} + L \cdot [\text{CH}_3\text{Br}] - L \cdot [\text{Br}_y]
\end{align*}
\]

Consider the atmosphere alone (designated case B1, no ocean). A steady state distribution forced from surface emissions of CH<sub>3</sub>Br is calculated by integrating the coupled diffusion equation (1) for several decades. The resulting profiles of CH<sub>3</sub>Br and Br<sub>y</sub> are shown by the thick lines in Figures 1a and 1b, respectively. This pattern is typical of the halocarbon source gases: well mixed tropospheric abundance, falling off slowly in the lower stratosphere and more rapidly in the upper stratosphere, coinciding with the release of Br<sub>y</sub> in the stratosphere such that the sum of mixing ratios, CH<sub>3</sub>Br + Br<sub>y</sub>, is constant through the stratosphere. The steady state lifetime of CH<sub>3</sub>Br, 1.75 years, is computed as the total abundance (157 kt for 10 ppt at the surface) divided by the mean annual loss (90 kt/yr), which at steady state balances emissions.

What happens if emissions cease? Consider a hypothetical case in which all sources responsible for 10 ppt of CH<sub>3</sub>Br are cut. Figure 1 follows the evolution of both profiles (thin lines, labeled with the year after cutoff). The CH<sub>3</sub>Br profile decays with a timescale of about 2 years and changes shape. The Br<sub>y</sub> profile maintains the same basic shape, does not change much over the first 2 years, and then decays much more slowly than does CH<sub>3</sub>Br. The CH<sub>3</sub>Br decay is summarized in Figure 2. It begins with a 1.75-year e-folding but asymptotically approaches a 2.1-year e-folding. The decay time for stratospheric Br<sub>x</sub>, however, is about 4.5 years. Neither of these decay times is reflected in the steady state lifetime. The decay patterns and their e-folding times are identical to the natural modes and their timescales [Prather, 1996] as derived in section 3.

Global lifetimes or individual reservoir turnover times are often mistakenly thought to be true timescales of the system's response to a perturbation. Figure 3 presents block diagrams of the CH<sub>3</sub>Br contents (kilolons) and fluxes (kilolons/yr) for three cases: B1, no ocean (Figure 1); H2, an oceanic sink but no source; and B3, an oceanic source to match the observed average 85% saturation. All numbers refer to a steady state with 10 ppt at the surface; see also Table 1. The global
3. Natural Modes of the \{CH$_3$Br, Br$_2$\} System

In atmospheric chemistry the continuity equation (2) for the concentration of each species at a given spatial location \(x_i\) can be expressed in terms of its local net chemical production \(p_i\) and its transport tendency \(\nabla \Phi\) (i.e., the flux divergence). We solve equation (2) for the mixing ratio, \(f_i = x_i/N\), where \(N\) is the concentration of background air. The index \(i\) covers \(m\) species at \(n\) spatial locations. The \(nm\times nm\) Jacobian matrix \(J\) (equation (3)) is defined as the partial derivative of each equation with respect to each independent variable. In a 1-D diffusion model the flux is down-gradient, \(\Phi = -K \Delta x/\Delta z\) (vertical dimension \(z\), diffusion coefficient \(K\)), and its divergence in equation (3) can be expressed as a finite difference equation involving nearest neighbors. The Jacobian matrix \(J\) is then block tridiagonal (equation (4)). The \(2\times2\) diagonal blocks \(P \cdot T\) include the real asymmetric chemical Jacobian plus the transport coefficients. The upper and lower diagonal blocks \(T\) are diagonal matrices with only transport coefficients (e.g., \(K/\Delta x^2\)). The boundary conditions \(B\) are matrices that couple species in the lowermost two layers and also, separately, the uppermost two layers.

\[
\begin{align*}
N \frac{df_i}{dt} &= dx_i/dt - p_i - \nabla \Phi_i \\
J_{ik} &= \frac{\partial (pf_i/N)}{\partial x_k} - \frac{\partial (\nabla \Phi_i/N)}{\partial f_k} \\
J &= \begin{bmatrix} B & B' & 0 & 0 & \ldots & 0 & 0 & 0 & 0 \\
B' & P+T & T' & 0 & \ldots & 0 & 0 & 0 & 0 \\
0 & T' & P+T & T'' & 0 & \ldots & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \ldots & 0 & T' & P+T & T'' \\
0 & 0 & 0 & 0 & \cdots & 0 & B' & B & B 
\end{bmatrix}
\end{align*}
\]

The \(nm\) eigenvectors of \(J\), \(A^k\), span the space of chemical species. The corresponding eigenvalues \(c_k\) describe the e-folding frequency (per second) of that eigenvector. Any species distribution \(S\) (i.e., vertical profiles of both CH$_3$Br and Br$_2$) can be expressed as a sum of these eigenvectors (natural modes) (equation (5)). The set \(A^k\) is linearly independent but unfortunately not orthogonal; hence, the complete set is needed to create the \(\Lambda\) matrix and solve for the coefficients of each mode, \(S_k = (A^k \cdot S)\). (If the \(A^k\) were orthogonal, then each coefficient \(S_k\) can be calculated from each \(A^k\) alone.) The decay of that distribution \(S\) is exactly the e-folding of the individual modes at their characteristic timescales of \(1/c_k\) (equation (6)).

\[
\begin{align*}
S(0) &= \sum_{k=1}^{nm} s_k A^k \\
S(t) &= \sum_{k=1}^{nm} s_k A^k e^{f(-c_k t)} 
\end{align*}
\]

For the \{CH$_3$Br, Br$_2$\} system without an ocean layer the \(J\) matrix (equation (4)) is \(28\times28\) (\(n=14\), \(m=2\)), and there are 28
Table 1. Analysis of Global Lifetimes at Steady State

<table>
<thead>
<tr>
<th></th>
<th>D1</th>
<th>B3/Sa</th>
<th>B3/O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$Br at 0 km, ppt</td>
<td>10.0</td>
<td>7.0</td>
<td>3.0</td>
</tr>
<tr>
<td>CH$_3$Br in ocean</td>
<td>---</td>
<td>4.5</td>
<td>4.0</td>
</tr>
<tr>
<td>(vapor pressure), ppt</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br$_2$ at 20 km</td>
<td>4.17</td>
<td>2.90</td>
<td>1.27</td>
</tr>
<tr>
<td>CH$_3$Br content</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stratosphere, kt</td>
<td>12.0</td>
<td>8.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Troposphere, kt</td>
<td>145.0</td>
<td>100.8</td>
<td>44.2</td>
</tr>
<tr>
<td>Ocean, kt</td>
<td>---</td>
<td>1.5</td>
<td>2.7</td>
</tr>
<tr>
<td>CH$_3$Br losses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stratosphere, kt/yr</td>
<td>1.6</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Troposphere, kt/yr</td>
<td>88.0</td>
<td>61.2</td>
<td>26.8</td>
</tr>
<tr>
<td>Ocean, kt/yr</td>
<td>---</td>
<td>45.3</td>
<td>76.7</td>
</tr>
<tr>
<td>CH$_3$Br emissions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface, kt/yr</td>
<td>89.6</td>
<td>107.6</td>
<td>---</td>
</tr>
<tr>
<td>Oceanic, kt/yr</td>
<td>---</td>
<td>---</td>
<td>104.0</td>
</tr>
<tr>
<td>Global lifetime against</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>loss in each reservoir</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stratosphere, years</td>
<td>98.</td>
<td>100.</td>
<td>101.</td>
</tr>
<tr>
<td>Troposphere and</td>
<td>1.78</td>
<td>1.81</td>
<td>1.89</td>
</tr>
<tr>
<td>soils, years</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ocean, years</td>
<td>---</td>
<td>2.44</td>
<td>0.66</td>
</tr>
<tr>
<td>Global lifetime (inverse</td>
<td>1.75</td>
<td>1.03</td>
<td>0.49</td>
</tr>
<tr>
<td>sum of above), years</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

aB3 (Figure 3) is split into surface (/S) and oceanic (/O) sources.

modes. Since the CH$_3$Br solution is independent of Br$_2$, one expects that only 14 modes describe the CH$_3$Br distribution, and indeed only 14 of the 28 modes have nonzero elements for CH$_3$Br. These modes as shown in Figure 4 (dimensionless, relative perturbations in the mixing ratio) can be combined uniquely to describe any vertical profile of CH$_3$Br. Short-lived modes are clearly associated with nearest-neighbor transport. The timescales of the stratospheric modes become slower in the lower stratosphere near the diffusion minimum. All of the modes change sign except the longest, primary mode which must have one sign since it is the final pattern that decays. In spite of these negative concentrations in each mode, the sum of modes corresponding to any positive distribution (equation (5)) remains positive throughout its decay (equation (6)). The primary 2.10-year mode represents the decay pattern of a gas that is photolyzed rapidly in the upper stratosphere and also removed quickly in the troposphere (see decay of CH$_3$Br profile in Figure 1a). Increasing the spatial resolution (i.e., degrees of freedom) leads to a corresponding increase in the number of short-lived modes corresponding to nearest-neighbor transport but does not substantially alter the primary mode.

For the (CH$_3$Br, Br$_2$) system with an ocean layer, the J matrix (equation (4)) is 30×30 (n=15, m=2), and there are 30 modes of which 15 describe CH$_3$Br patterns as shown in Figure 5. Comparing Figures 4 and 5, one can identify the additional mode (0.021 years) that is most closely associated with the ocean layer (labeled -4 km). All other modes look similar to the atmosphere-alone case. The addition of a degree of free-tom (the ocean layer) shifts many but not all of the modes and creates a new one that is not just the ocean chemical turnover time (~0.03 years), but a coupling of that with the atmospheric reservoir. Timescales for the nearest neighbor transport are unchanged. With this additional sink those modes representing more global patterns, such as the primary mode, have a shorter timescale, 1.83 versus 2.10 years. The modes couple all reservoirs and chemical losses, and thus, the patterns cannot always be identified uniquely with the additional component.

![Figure 4](image-url). The complete set of 14 natural modes for CH$_3$Br in the case with no ocean (case B1). Each vertical pattern in the mixing ratio of CH$_3$Br from 0 to 52 km is dimensionless and labeled with its corresponding timescale.
Figure 5. The complete set of 15 natural modes for CH$_3$Br in the case with an ocean sink (cases B2 and B3). Each vertical pattern in the mixing ratio of CH$_3$Br from -4 km (ocean layer) to 52 km is dimensionless and labeled with its corresponding timescale.

Figure 6. Decomposition of a steady state distribution (SS) of CH$_3$Br (parts per trillion) and Br, (parts per trillion) into natural modes. The steady state is forced by both surface and oceanic emissions to achieve 1 ppt CH$_3$Br in the lower atmosphere and 85% saturation in the ocean (case B3). Each scaled mode (parts per trillion) is multiplied by the coefficient derived from the SS distribution and is labeled with its e-folding timescale. Two of the Br, modes (0.892 and 0.912 years) are nearly degenerate and have been combined.
The steady state distribution (SS) of CH₂Br and Br₂ resulting from a combination of surface and oceanic emissions (B3) is shown in Figure 6. The source was scaled to give 1 ppt of CH₂Br in the lower atmosphere and 85% saturation in the ocean layer. These profiles are shown with the open symbols in the left-hand panels. The SS:CH₂Br profile is comprised of all the 15 modes in Figure 5, but only those with significant coefficients sⁿ are shown as scaled modes (in units of parts per trillion) in Figure 6. Except for the stratospheric-readjustment mode (0.497 years), the SS profile is predominantly a combination of the two longer-lived modes (0.912 and 1.831 years). The SS:Br profile is comprised of the full 30 modes (not shown), and those with the largest coefficients sⁿ are shown here. Some of these scaled modes (0.387, 0.89, and 4.519 years) are unique to Br₂ and have no CH₂Br elements. The 0.89 year and 0.91-year modes have been combined since they are nearly degenerate with large and cancelling coefficients. The primary 4.519-year mode represents the removal of a conserved trace gas from the stratosphere (compare with decay profile in Figure 1b). Note that this long-lived mode has amplitude 2 ppt in the upper stratosphere, being balanced by negative mixing ratios from the other modes, and explains why the profile of Br₂ in Figure 1b hardly changes in the first 2 years.

Once the A matrix of modes has been calculated as in Figure 5, the exact, time-dependent response to any perturbation may be readily derived. Consider a single, pulsed emission equivalent to a surface source (all CH₂Br in the 0-km atmospheric layer, labeled PE:CH₂Br in the left panel of Figure 7). This profile has been scaled to have the same total content as SS:CH₂Br in Figure 6, and the scaled modes (units of parts per trillion) comprising PE:CH₂Br are shown with their timescales. Two short-lived modes (0.004 and 0.007 years) represent rapid tropospheric mixing; others involve exchange with the ocean layer, and the three longest-lived modes are similar to those for SS:CH₂Br but with different amplitudes.

The CH₂Br modes shift smoothly with changes in the chemical model. For example, if Yvon and Butler's [1996] updated mean oceanic loss of 15%/d for CH₂Br is used, the timescales of the two major modes shift from 1.83 to 1.81 years and from 0.91 to 0.82 years. The steady state lifetime for surface emissions drops from 1.03 to 0.91 years. Assuming 20% undersaturation of CH₂Br in the ocean layer, the implied surface emissions of 113.5 kyr maintain an atmospheric abundance of 6.5 ppt at 0 km (versus 7.1 ppt in case B3), and oceanic sources maintain a background level of 3.5 ppt.

4. ODPs and the Transient Response

The ozone depletion potential (ODP) for a halocarbon is meant to measure the cumulative environmental impact (i.e., O₂ depletion) from a single release of a gas ratioed to that from an equal release of CFC₁₂. Instead of being computed as the true transient response following release of the gas, this cumulative impact is assumed to be the product of (1) the global-mean steady state lifetime and (2) the steady state concentration of active chlorine/bromine in the stratosphere corresponding to the amount of source gas emitted [e.g., WMO, 1995]. This approximation is rigorously correct as proven by Prather [1996], although the timescale is misleading as seen in Figure 1, and further, the steady state lifetime must be calculated using the comparable emission pattern.

The true transient response of CH₂Br or Br₂ can be written exactly for any altitude in terms of the modes (equation (6)) for decay from SS (Figure 6) or for evolution of a pulsed emission (PE, Figure 7). For most assessments or policy options the focus is on the perturbation (positive or negative) caused by a change in emissions (positive or negative) for a given year-long PE. Any combination of actions, including a long-term change in emissions, can be expressed as a sum of PE cases.

The PE transients give the history of a single pulse, which is meant to be integrated by the ODP. CH₂Br at 0 km (equation (7)) begins at 3.38 ppt and evolves as a mix of rapidly and more slowly decaying terms that integrate (product of coefficients and timescales, t/c, to 1.03 ppt yr. The coefficients of each exponential in equation (7) are the 0-km values in Figure 7. The content is scaled to the steady state profile of 1 ppt. A theorem equates the integral to the SS lifetime multiplied by the SS mixing ratio [Prather, 1996]. The correct lifetime is 1.03 years. Indeed, the corresponding equation for the SS CH₂Br at 0 km (from Figure 6) can be easily calculated by integrating over an infinite prehistory of emissions, that is multiplying the coefficient in equation (7) by the e-folding time and dividing by 1.03. Stratospheric Br₂ (20 km) begins at 0.00 ppt with a large number of cancelling terms. The rapid decay of some negative coefficients leads to a rising concentration which eventually decays with the 4.52-year mode (equation (8)). The integral of the Br₂ transient is 0.43 ppt yr, which equals 1.03 years multiplied by 0.417 ppt (the SS Br₂ at 20 km for 1 ppt CH₂Br in the lower atmosphere). The reason that this same theorem appears to work for Br₂ using the CH₂Br lifetime is due to the complementary nature of CH₂Br and Br₂ in the stratosphere.

\[
\begin{align*}
\text{CH₂Br}^{\text{PE}}(t, 0 \text{ km}) &= 0.060c^{0.831t} + 0.964c^{0.912t} \\
&+ 0.029c^{0.497t} + 0.522c^{0.891t} + 0.300c^{0.0018t} \\
&+ 0.885c^{0.007t} + 0.644c^{0.0004t} \quad \text{ppt} \\
\text{Br₂}^{\text{PE}}(t, 20 \text{ km}) &= 0.273c^{0.451t} - 0.818c^{0.811t} \\
&+ 10.75c^{0.912t} - 10.187c^{0.892} - 0.217c^{0.497t} \\
&+ 0.247c^{0.38t} - 0.096c^{0.451t} + 0.045c^{0.0017t} \quad \text{ppt}
\end{align*}
\]
Figure 8 shows the transient response of Br\textsubscript{2} at 20 km to a single release of CH\textsubscript{3}Br equal in mass to the steady state distribution with a surface mixing ratio of 1 ppt (equation (8)). More than 99\% of the tropospheric CH\textsubscript{3}Br is lost in the 5 years following emission. Stratospheric Br\textsubscript{2} levels just begin to peak then. About 25\% of the O\textsubscript{3} depletion occurs more than 10 years after the emission of CH\textsubscript{3}Br. The corollary is that a cut in CH\textsubscript{3}Br emissions yields recovery of O\textsubscript{3} only on a timescale of 5 to 15 years. The typical approach in calculating the halogen loading of the stratosphere [Prather and Watson, 1990] or the time-dependent ODP [Solomon and Albright, 1992] is to shift the steady state pattern by 2 to 3 years to account for the delay in the source gas reaching the stratosphere (as calculated by WMO [1995, Figures 13-5 and 6]). However, for short lived gases such as CH\textsubscript{3}Br and for short time horizons this shift does not accurately account for the slow build up and decay of the ozone-depleting products in the stratosphere and can greatly overestimate the time-dependent ODP for horizons less than 10 years.

5. Timescales and Steady State

Natural modes are a mathematically rigorous, fundamental property of the chemical-transport system (i.e., current atmosphere) and do not depend on the manner of perturbation. Exponential decay of each natural mode with its own timescale is an exact solution in the limit of linear behavior. A unique mixture of modes is excited by any perturbation. For tightly coupled nonlinear chemical systems such as (CH\textsubscript{3}H\textsubscript{2}, C\textsubscript{O}, OH) the use of natural modes clearly defines the timescales and shows how perturbations to one species couple across all. For the simple atmospheric chemistry of the (CH\textsubscript{3}Br, Br\textsubscript{2}) system here the timescales of transport and chemistry are combined into the timescales of the long-lived, global modes. These modes, in various combinations, describe most transient and steady state responses to varied patterns of emissions. Because of this simple behavior, identification of the natural modes in current multi-dimensional atmospheric chemistry-transport models, while extremely difficult, would be valuable in diagnosis and also for prediction.

The steady state lifetime and distribution can be defined in terms of the natural modes. CH\textsubscript{3}Br provides a stunning example of how this steady state depends on the manner of forcing. For the atmosphere alone (B1), using Table 1 and Figure 3, the lifetimes of CH\textsubscript{3}Br against stratospheric loss (98 years) and tropospheric loss (1.78 years) combine to give the total steady state lifetime for a distribution forced by surface emissions (1/2 years = inverse of the sum of inverses). For the more realistic case with both surface and oceanic emissions (B3) the two different sources can be separated using case B2. In Table 1 the lifetimes split B3 into that component due to surface emissions (7 ppt at 0 km) and that due to oceanic emissions (3 ppt at 0 km). (This result is based on the assumed saturation, exchange rates, etc. in the 1-D model and is not intended to be the best current assessment.) Using the contents and fluxes associated with each source (including the oceanic content), the CH\textsubscript{3}Br lifetime for surface emissions is 1.03 years as before, but for oceanic emissions it is only 0.49 years. An oceanic source puts more CH\textsubscript{3}Br in the reservoir with the most rapid destruction. Amazingly, both B3/surface and B3/ocean, with lifetimes differing by a factor of 2, are represented by the same modes and timescales including the long-lived decay modes of 0.91 and 1.83 years, but with different coefficients.

If the (CH\textsubscript{3}Br, Br\textsubscript{2}) analysis is extended to longer-lived halogen source gases such as CH\textsubscript{2}CCl\textsubscript{2}, or even those without a tropospheric sink such as CFCl\textsubscript{3}, the discrepancy between the time scale for ozone recovery and that inferred from the steady state lifetime becomes less. This convergence of the lifetime and the primary mode’s time scale happens as the global mean lifetime (e.g., 50 years for CFCl\textsubscript{3}) becomes much longer than the slowest transport time scale (e.g., 3-5 years for stratospheric removal). We are now observing the decay of atmospheric CH\textsubscript{2}CCl\textsubscript{2} following the recent phaseout in production [Prinn et al., 1995; Montzka et al., 1996]. This e-folding time is coincidently expected to be almost identical to the derived steady state lifetime based on surface emissions [Prinn et al., 1995], and we may observe a small residual maximum in the high-latitude lower stratosphere as CH\textsubscript{2}CCl\textsubscript{2} decays in the atmosphere. For longer-lived gases like CFCl\textsubscript{3}, the timescale of the primary mode is a few percent less than the lifetime at steady state for surface emissions.

The long-lived, odd-nitrogen source gas N\textsubscript{2}O, however, is expected to have natural modes and timescales that are significantly shorter than the steady state lifetime because of the photochemical coupling in the (N\textsubscript{2}O, NO\textsubscript{2}, O\textsubscript{3}) system. A preliminary study with this 1-D model that includes coupling of NO\textsubscript{2} with O\textsubscript{3} depletion and subsequent increased photolysis of N\textsubscript{2}O indicates that N\textsubscript{2}O perturbations may damp at a rate 10-20% faster than the lifetime.
Appendix

A 1-D chemical diffusion model of \{CH, Br, Br\_2\} for the atmosphere [Logan et al., 1978; Prather, 1994] is as follows: mixing ratios solved for at 14 altitudes, \( z = 0 - 4 - 8 - 12 - 16 - 20 - ... - 52 \text{ km}; \) density given by \( N = 2.4\times 10^6 \text{ p cm}^{-3} \) assuming \( p = 1000 \times 10^6 \text{ mb} \) (note that \( N \) needs to be scaled by 1.25 for global mean atmospheric mass); diffusion coefficient, \( K = 3\times 10^7 \text{ cm}^2 \text{ s}^{-1} \) for 0 - 12 km; \( K = 3\times 10^7 \text{ cm}^2 \text{ s}^{-1} \) at 14 km, increases as 1/p above; chemical loss of CH, \( L_C = 2.16\times 10^7 \text{ s}^{-1} \) from 0-10 km ("OH loss" at 1/1.46 per year); \( L_C = 6\times 10^7 \text{ s}^{-1} \) above 10 km (constant above \( p = 1 \)); chemistry of Br, every loss of CH,Br produces Br; \( L_B = 2.31\times 10^5 \text{ s}^{-1} \) from 0-10 km ("rainout" at 1/5 per day); numerics, 2nd-order finite difference, 2nd-order boundary conditions, implicit in time (single-step solution for steady state). The model of \{CH, Br\_2\} for the ocean [Lobert et al., 1995] is as follows: ocean box (mixed layer) connected to surface atmospheric layer (0.2 km); effective thickness based on solubility and mixed layer depth, 0.5x10^5 \text{ cm}^2 (versus 4.8x10^5 \text{ cm}^2 for 0-2 km layer); effective air exchange rate with atmosphere, 3.86x10^5 \text{ cm}^2 \text{ s}^{-1}; chemical loss of CH,Br, 9.26x10^5 \text{ s}^{-1} (8%/day). Three sample cases are shown (Figure 3): B1, atmosphere alone, 10 ppt CH,Br @ 0 km, 4.17 ppt Br @ 20 km (all cases); R2, atmosphere plus ocean, only surface CH,Br source (ocean at 45% saturation); B3, atmosphere plus ocean, surface and oceanic CH,Br sources (ocean at 85% saturation).

Acknowledgments. This research was supported by NASA's Atmospheric Chemistry Modeling and Analysis Program and NSF's Atmospheric Chemistry Program. I thank R. Cicerone, B. Harnegar, S. Olsen, and anonymous reviewers for helpful comments.

References


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