Lifetimes and time scales in atmospheric chemistry

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Atmospheric composition is controlled by the emission, photochemistry and transport of many trace gases. Understanding the time scale as well as the chemical and spatial patterns of perturbations to trace gases is needed to evaluate possible environmental damage (e.g. stratospheric ozone depletion or climate change) caused by anthropogenic emissions. This paper reviews lessons learned from treating global atmospheric chemistry as a linearized system and analysing it in terms of eigenvalues.

The results give insight into how emissions of one trace species cause perturbations to another and how transport and chemistry can alter the time scale of the overall perturbation. Further, the eigenvectors describe the fundamental chemical modes, or patterns, of the atmosphere’s chemical response to perturbations.

Keywords: atmospheric chemistry; time scales; lifetimes; chemical modes; eigenvalues

1. Introduction to time scales

Knowledge of time scales in the Earth system has both scientific and practical applications. Chemical feedbacks in the atmosphere, for example, have been shown to extend the duration of methane perturbations (Prather 1994), thus increasing the climate impact of (and the Kyoto tax on) emissions of this greenhouse gas by 40% (IPCC 1996). Emissions of trace gases with lifetimes of a day, such as nitrogen oxides, are now predicted to perturb other greenhouse gases for decades (Derwent et al. 2001; Wild et al. 2001). Stratospheric aerosols from major volcanic eruptions mostly disappear from the atmosphere in a couple of years, yet we see decadal dips in global mean sea level resulting from their brief cooling of the Earth (Church et al. 2005). This paper summarizes a methodology developed over the last decade for analysing atmospheric chemistry through linearization and eigenvalue analysis. This new formalism accounts for the chemical feedbacks, describes the long temporal response to apparently short-lived perturbations, integrates over the environmental impacts of trace gas emissions, but requires us to replace our traditional view of lifetimes in atmospheric chemistry.

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One contribution of 18 to a Discussion Meeting Issue ‘Trace gas biogeochemistry and global change’.
A typical trace gas that mixes throughout the atmosphere and into the ocean and terrestrial biosphere encounters a wide range of biogeochemical conditions, each with a different reactivity. Integrating the global loss of a trace gas \( \dot{L}, \text{kg yr}^{-1} \) and dividing it into the global burden \( B, \text{kg} \) of the gas yield a single number with units of time \( T, \text{yr} \), which has been called the lifetime or residence time (Bolin & Rodhe 1973; O’Neill et al. 1994). When the global source \( S, \text{kg yr}^{-1} \) equals the loss over a year, the trace gas is in steady state, and the lifetime \( T_{SS} = B / \dot{L} = B / S \) is often thought of as a constant for the current atmosphere, a universal value that defines properties such as atmospheric variability (Junge 1974). Such lifetimes are used to provide a time scale for environmental impacts, including ozone depletion and global warming potentials (ODP and GWP). While this calculated lifetime has units of time, it is most often not a true time scale of the system and, for gases with short lifetimes, fails to identify the long duration of some impacts.

This paper develops the concept of atmospheric chemistry as a coupled system across different trace species with transport between different regions and radiative feedbacks. These three processes, individually or together, lead automatically to the new expectation that a perturbation to one species in one location will invoke a global response on a wide range of time scales, probably involving other chemical species.

The eigenvalue decomposition of a properly discretized and linearized chemistry–transport system produces eigenvectors that are perturbation patterns of trace gas abundances, also known as chemical modes. The negative inverse of the eigenvalue of each chemical mode is the time scale for the mode to decay by a factor of \( e \). The derivation of these and related properties is presented in §2. Simple one-box examples for stratospheric ozone and tropospheric methane are given in §§3 and 4, respectively. Section 5 shows how the time scale for methyl bromide is altered by transport exchange between the stratosphere and the troposphere. Ozone interacts with other gases through control of the transmission of solar ultraviolet, and this radiative coupling changes the time scale for nitrous oxide as shown in §6. Section 7 reviews the special role of steady-state lifetime as an integrator of environmental impacts. Continuous semi-infinite systems are considered briefly in §8. Observations of the stratospheric decay mode are presented in §9. The existence of global chemical modes in realistic three-dimensional models is discussed in §10. Future applications are addressed in §11.

2. Atmospheric chemistry: linearization, time scales and chemical modes

The continuity equation describing the instantaneous rate of change in abundance \( V \) of trace gas \( n \) at location \( (x, y, z) \) can be expressed as

\[
\frac{dV(x, y, z, n)}{dt} = \text{Chem}[V(x, y, z, n')] + \text{Tran}[V(x', y', z', n)] + \text{Rad}[V(x', y', z', n'')],
\]

where the chemistry operator (Chem) couples all trace species \( n' \) but is local, the transport operator (Tran) does not interchange species but is global \( (x'', y'', z'') \) and the radiation operator (Rad) couples the trace gas to a global distribution of a few species \( n'' \), e.g. ozone and aerosols). Under most circumstances, the time scales of perturbations to atmospheric composition can be derived from the eigenvalues of the linearized form of this continuity equation.
Assume that $V$ is a solution for a generic operator $A$, $dV/dt = A[V]$, then the continuity equation for a perturbation $\delta V$ can be derived as

$$\frac{d\delta V}{dt} = \frac{d[V + dV]}{dt} - \frac{dV}{dt} = A[V + \delta V] - A[V] = J_V \cdot \delta V + \text{order}(\delta V^2),$$

where the Jacobian matrix $J$ of the operator $A$ is the first term in the Taylor expansion of $A[V + \delta V]$ evaluated at $V$, i.e. the linearized system (e.g. Prather 1996, 2002; Manning 1999). The Jacobian matrix has dimension $m \times m$, where $m$ is the number of variables. Species are inherently discrete, and adopting a discrete spatial grid gives us a finite number of variables across $(x, y, z, n)$. For discussion of the continuum, see §8.

If the perturbation $\delta V$ is an eigenvector of $J_V$ with eigenvalue $\lambda$, then

$$\frac{d\delta V}{dt} = J_V \cdot \delta V = \lambda \delta V,$$

and the exact solution is $\delta V(t) = \delta V(0) \exp(\lambda t)$. In general, there will be a set of $m$ linearly independent eigenvectors $E_i$, each with eigenvalue $\lambda_i (yr^{-1})$. For stable systems, all $\lambda_i$ must be less than or equal to zero. The inverse negative eigenvalue is the mode time ($T_i = -1/\lambda_i$) determining the e-fold of the chemical mode. The $E_i(x, y, z, n)$ are dimensionless and represent a relative pattern of trace species, both in space and across species. Any perturbation can be expressed as a unique linear combination, $\delta V(0) = \sum_{i=1}^{m} a_i E_i$, with an exact solution $\delta V(t) = \sum_{i=1}^{m} a_i E_i \exp(\lambda_i t)$. In this case, the coefficients $a_i$ have abundance units (kg) and each $E_i$ has a scalar mass coefficient for each species $(n)$, defined as $m^i_n$ that sums over the eigenvector's spatial distribution of $(n)$. The total mass of species $(n)$ in a perturbation can be represented by the mass operator $M^n[\delta V] = \sum_{i=1}^{m} a_i m^i_n$ (kg).

The recognition that any perturbation to atmospheric composition can be expressed as a sum of chemical modes, each with a fixed decay term, has several important applications (Prather 1994). First, the e-folding times $T_i$, rather than the budget-derived lifetime $T_{SS}$, are the true time scales of variability in the system. Second, the asymptotic approach to a steady state becomes a single exponential decay with the largest $T_i$. In practical terms, this recognition has saved large amounts of computing time, since perturbations (e.g. adjustments to a new steady state, or model response functions for inverting emission sources) can be readily and accurately extrapolated. Third, a chemical mode, in general, will couple across different species, and thus a perturbation to any species should be expected to excite all modes and respond on the full range of time scales in the system. Perturbation dynamics developed by Farrell & Ioannou (2000) has extended this approach to determining which types of perturbations produce the greatest impact on a chosen species at a chosen site.

3. Stratospheric ozone chemistry: the definition of ‘odd oxygen’

In the upper stratosphere, the Chapman (1930) mechanism, which includes only atomic oxygen (O), ozone (O$_3$) and molecular oxygen (O$_2$), roughly describes the abundance of ozone. Additional reactions involving others species (e.g. HO$_2$, NO, Cl) are needed to accurately match the observed profile and trends. When solving the continuity equations for O and O$_3$, researchers recognized that O$_3$ perturbations behaved as an empirically defined ‘odd oxygen’ (O + O$_3$) rather
than independently as O and O₃. Eigenvalue decomposition of the Chapman mechanism readily derives the correct time scales and shows that odd oxygen is indeed one of the fundamental perturbation patterns of this chemical system.

The Chapman reactions, their rates and coefficients typical of 42 km altitude at mid-latitudes can be summarized as

(i) \( O₂ + \text{photon} \Rightarrow O + O \quad R₁ = J₁[O₂] \quad J₁ = 1.8 \times 10⁻¹⁰ \text{ s}⁻¹ \)

(ii) \( O + O₂(,+M) \Rightarrow O₃(+M) \quad R₂ = k₂[O][O₂] \quad k₂ = 5.26 \times 10⁻¹⁷ \text{ cm}³ \text{ s}⁻¹ \)

(iii) \( O₃ + \text{photon} \Rightarrow O₂ + O \quad R₃ = J₃[O₃] \quad J₃ = 1.4 \times 10⁻³ \text{ s}⁻¹ \)

(iv) \( O + O₃ \Rightarrow O₂ + O₂ \quad R₄ = k₄[O][O₃] \quad k₂ = 3.0 \times 10⁻¹⁵ \text{ cm}³ \text{ s}⁻¹ \)

For this abbreviated set of reactions, the chemical rate equations for the densities of atomic oxygen, ozone and molecular oxygen are

\[
\frac{d[O₃]}{dt} = R₂ - R₃ - R₄
\]
\[
\frac{d[O]}{dt} = 2R₁ + R₃ - R₂ - R₄
\]
\[
\frac{d[O₂]}{dt} = 2R₄ + R₃ - R₁ - R₂,
\]

and the Jacobian elements are

\[
\]

The steady-state solution for this example is \([O] = 1.26 \times 10⁹ \text{ cm}⁻³\), \([O₃] = 6.55 \times 10¹¹ \text{ cm}⁻³\) and \([O₂] = 1.38 \times 10¹⁶ \text{ cm}⁻³\). Lifetimes in atmospheric chemistry are traditionally defined in terms of a linearized loss frequency (units of s⁻¹) or, equivalently, the ratio of abundance (e.g. number cm⁻³) divided by a production or loss rate (cm⁻³ s⁻¹). For the Chapman mechanism at 42 km, we can derive the following possible lifetimes:

\[
T(O₂) = \frac{[O₂]}{R₁} = 176 \text{ yr}
\]
\[
T(O₃) = \frac{[O₃]}{(R₃ + R₄)} = 12 \text{ min}
\]
\[
T(O) = \frac{[O]}{(R₂ + R₄)} = 1.4 \text{ s}
\]
\[
T(O + O₃ \equiv Oₓ) = \frac{[O + O₃]}{2R₄} = 1.5 \text{ day}
\]
\[
T(\text{total O}) = \frac{[O + 2O₂ + 3O₃]}{0} = \text{infinity}.
\]

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Molecular oxygen photolyses with an e-fold time scale of 176 yr, ozone photolyses with a time scale of 12 min and atomic oxygen reacts with O$_2$ on a time scale of 1.4 s. These three time scales are the negative inverse of the diagonal elements of the Jacobian of the three continuity equations above. We can define additional time constants for total oxygen and odd oxygen. As expected, the abundance of total oxygen is constant (i.e. $d(\text{[O]} + 2\text{[O}_2] + 3\text{[O}_3])/dt=0$) and hence has a time scale of infinity. The odd oxygen time-scale, 1.5 day, is determined by recombination of O and O$_3$ ($R_4$).

Which of these five time scales accurately describes this system? The Jacobian matrix derived from the 3×3 system of equations above has one zero eigenvalue and two non-zero eigenvalues of $-1/(1.4\text{ s})$ and $-1/(0.74\text{ day})$. The zero eigenvalue is consistent with the infinite time scale for changing total oxygen, the next larger eigenvalue is close to that for odd oxygen and the largest eigenvalue closely matches the O lifetime. The chemical mode (eigenvector) with mode time of 1.4 s is $([\text{O}_3], [\text{O}], [\text{O}_2]) = (-0.995, +1.000, +0.992)$ and that with mode time of 0.74 day is $(+1.0000, +0.0019, -1.5010)$. Perturbations to the ratio $[\text{O}] : [\text{O}_3]$ disappear quickly with the time scale of O recombination ($R_2$), whereas those to the sum $[\text{O}] + [\text{O}_3]$ decay more slowly. This latter odd oxygen mode preserves the ratio, $[\text{O}] : [\text{O}_3] = 0.0019$, of the steady-state solution.

We have lost the O$_2$ and O$_3$ time scales and have preserved only the largest eigenvalue (shortest time scale). The photolysis time for O$_3$ is not a time scale of this system! This is typical of coupled systems: the largest diagonal terms remain as eigenvalues, and the smaller ones are altered. The eigenvalue decomposition gives a mode time that is a factor of two smaller than $T(\text{O}_X)$. Since at least the 1970s, atmospheric chemistry modelling has recognized that stratospheric O$_3$ responded to perturbations more slowly than the photolysis time scale, and researchers effectively intuited the eigenvalue decomposition by defining $\text{O}_X$ with its time-scale. The decomposition, however, includes the effect of quadratic loss of $\text{O}_X$ and has the correct time scale, $[\text{O}_X]/4R_4$.

4. Tropospheric methane chemistry: delayed recovery of a perturbation

The conundrum presented by Don Fisher in 1993 at a workshop on stratospheric ODP led to the discovery that chemical coupling of methane (CH$_4$), carbon monoxide (CO) and hydroxyl radicals (OH) would extend the effective lifetime of atmospheric CH$_4$ perturbations. Using a two-dimensional global chemistry–transport model (CTM), Fisher (1995) reported that a pulse of CH$_4$ added to the atmosphere did not decay with the expected e-fold time equal to the CH$_4$ steady-state lifetime (e.g. 8 yr), but with one that was notably longer (e.g. 12 yr). Moreover, the time scale of this delayed recovery was constant, independent of the magnitude of the perturbation, indicating that a nonlinear chemical response was not the cause. Earlier, Isaksen & Hov (1987) had noted the importance of the CH$_4$–OH feedback in a global model, when a small increase (e.g. 10%) in global CH$_4$ emissions produced a larger relative increase (e.g. 14%) in steady-state CH$_4$ abundance. These phenomena were generally regarded as the result of a nonlinear response that would disappear for small perturbations. The formal relationship between the steady-state feedback and Fisher’s time scales was not immediately recognized.
In response to Fisher’s problem, Prather (1994, 1996) developed a simple one-box chemistry model that demonstrated how chemical feedbacks could alter the time scale of CH$_4$ perturbations. Manning (1999) updated this model and applied it to carbon isotopes, but in this example, the original box model is retained. Consider a simplified model of the CH$_4$–CO–OH chemical system as having three reactions

(i) CH$_4$ + OH ⇒⋯⇒ CO \hspace{1cm} R_5 = k_5[CH$_4$][OH] \hspace{1cm} k_5 = 1.266 \times 10^{-7} \text{ s}^{-1} \text{ ppt}^{-1}

(ii) CO + OH ⇒⋯ \hspace{1cm} R_6 = k_6[CO][OH] \hspace{1cm} k_6 = 5.08 \times 10^{-6} \text{ s}^{-1} \text{ ppt}^{-1}

(iii) OH + X ⇒⋯ \hspace{1cm} R_7 = k_7[X][OH] \hspace{1cm} k_7[X] = 1.062 \text{ s}^{-1},

and three constant source terms (parts per trillion (ppt) = picomoles per mole; parts per billion (ppb) = nanomoles per mole):

\[ S_{\text{CH}_4} = 177 \text{ ppb yr}^{-1} \quad S_{\text{CO}} = 240 \text{ ppb yr}^{-1} \quad S_{\text{OH}} = 1464 \text{ ppb yr}^{-1}. \]

Reaction (5) has intermediate steps (not shown) that produce CO. The X in reaction (7) is a class of species that are an important sink for OH. The continuity equations are

\[
\frac{d[\text{CH}_4]}{dt} = S_{\text{CH}_4} - R_5
\]

\[
\frac{d[\text{CO}]}{dt} = S_{\text{CO}} + R_5 - R_6
\]

\[
\frac{d[\text{OH}]}{dt} = S_{\text{OH}} - R_5 - R_6 - R_7.
\]

The rate coefficients and source terms are chosen to represent average tropospheric conditions and give steady-state abundances typical of the current atmosphere:

\[
[\text{CH}_4] = 1704 \text{ ppb} \quad [\text{CO}] = 100 \text{ ppb} \quad [\text{OH}] = 0.026 \text{ ppt}.
\]

The Jacobian (\(J\)) of the chemical system is calculated from

\[
J = \begin{pmatrix}
\frac{\partial \left( \frac{d[\text{CH}_4]}{dt} \right)}{\partial [\text{CH}_4]} & \frac{\partial \left( \frac{d[\text{CH}_4]}{dt} \right)}{\partial [\text{CO}]} & \frac{\partial \left( \frac{d[\text{CH}_4]}{dt} \right)}{\partial [\text{OH}]}

\frac{\partial \left( \frac{d[\text{CO}]}{dt} \right)}{\partial [\text{CH}_4]} & \frac{\partial \left( \frac{d[\text{CO}]}{dt} \right)}{\partial [\text{CO}]} & \frac{\partial \left( \frac{d[\text{CO}]}{dt} \right)}{\partial [\text{OH}]}

\frac{\partial \left( \frac{d[\text{OH}]}{dt} \right)}{\partial [\text{CH}_4]} & \frac{\partial \left( \frac{d[\text{OH}]}{dt} \right)}{\partial [\text{CO}]} & \frac{\partial \left( \frac{d[\text{OH}]}{dt} \right)}{\partial [\text{OH}]}
\end{pmatrix}
\]
and at steady state has the value (all units are yr\(^{-1}\))

\[
J = \begin{pmatrix}
-0.104 & 0 & -6.81 \times 10^6 \\
+0.104 & -4.17 & -9.23 \times 10^6 \\
-0.104 & -4.17 & -56.4 \times 10^6
\end{pmatrix}
\]

The diagonal elements are the negative inverse of the traditionally defined lifetimes

\[
9.6 \text{ yr (CH}_4\text{)} \quad 0.240 \text{ yr (CO)} \quad 0.56 \text{ s (OH)}.
\]

The three inverse negative eigenvalues (mode times) of \( J \) differ from these lifetimes owing to the chemical coupling (i.e. the off-diagonal terms)

\[
13.6 \text{ yr} \quad 0.285 \text{ yr} \quad 0.56 \text{ yr}.
\]

The corresponding eigenvectors are shown in figure 1. Given the relative species abundances in each mode and the mode time of each, one can easily identify the first as the CH\(_4\)-like chemical mode but with a time scale 40% longer than the CH\(_4\) lifetime, the second as the CO-like chemical mode with a 20% longer time scale and the third as the OH-dominated mode with a time scale equal to the OH lifetime. In this case, chemical coupling (i.e. off-diagonal terms in \( J \)) has shifted the smallest two eigenvalues, but left the time scale of the most rapid process unchanged.

A 1 ppb perturbation to CH\(_4\) alone can be decomposed into modes using the inverse of the eigenvector matrix. It is composed of 0.995 ppb in the first mode, 0.005 ppb in the second and less than 0.001 ppb in the extremely short-lived third mode. The analytical solution is then

\[
\delta[\text{CH}_4](t) \approx +0.995 \ e^{-t/13.6} + 0.005 \ e^{-t/0.285} \ ppb,
\]

Figure 1. Three eigenvectors of the CH\(_4\)-CO–OH system (see text) are labelled with their mode times. For each vector, the bars indicate the perturbation in absolute abundance (e.g. ppb). Each mode is scaled to have the maximum perturbation as +1 ppb. The amplitude of the OH perturbation for the first two modes is less than \(10^{-7}\) and does not show. (a) No. 1, 13.6 years, (b) no. 2, 0.285 years and (c) no. 3, 0.56 s.
and thus most of the perturbation decays with the 13.6-yr mode time. Since the long-lived mode also has CO and OH components, the other species also have decadal perturbations:

\[
\delta[\text{CO}](t) = +0.035 \ e^{-t/13.6} + 0.035 \ e^{-t/0.285} \ \text{ppb}
\]

\[
\delta[\text{OH}](t) = -4.5 \times 10^{-6} \ e^{-t/13.6} \ \text{ppt}.
\]

Likewise, a 1 ppb perturbation to CO alone excites all the three modes. The 0.15 ppb perturbation to CH$_4$ caused by the chemical coupling is initially masked but appears as the bulk of the CO perturbation decays in a few months. It decays with the characteristic 13.6-yr mode time:

\[
\delta[\text{CO}](t) = +0.005 \ e^{-t/13.6} + 0.995 \ e^{-t/0.285}
\]

\[
\delta[\text{CH}_4](t) = +0.15 \ e^{-t/13.6} - 0.15 \ e^{-t/0.285}.
\]

Can this help us understand Fisher’s results? The amount of CH$_4$ added to the model atmosphere was small enough that OH did not change by more than a few per cent. Thus, if the added CH$_4$ could be tagged, we would see it decay with the expected lifetime of 8 yr. However, the background CH$_4$ increased in response to the lowered OH, and thus the apparent decay rate for total CH$_4$ is the mode time of 12 yr (figure 2). The Isaksen and Hov results can be understood if one accepts that while the steady-state lifetime for the global CH$_4$ burden is about 8 yr, that for additional emissions is 12 yr (see also §7). The simple model above, when confirmed by the three-dimensional atmospheric chemistry models, resulted in a +40% revision to the IPCC’s GWP for CH$_4$ (Prather et al. 1995; Ramaswamy et al. 2001).
5. Time scales for methyl bromide: transport between reservoirs

Methyl bromide (CH$_3$Br), an ozone-depleting substance (ODS), is emitted into the atmosphere through natural, primarily oceanic, processes. Over the past few decades, humans have increased its atmospheric abundance through synthetic production and use as a fumigant for agricultural fields, structures and harvested crops. In the atmosphere, CH$_3$Br is lost with time scales of order a year through reaction with OH and by photolysis in the stratosphere. It delivers inorganic bromine (Br$^-$) to the stratosphere, where Br-catalysed reactions destroy O$_3$. There has been confusion (e.g. Butler 1994) over the definition of lifetime for a gas like CH$_3$Br with multiple reservoirs and further misunderstanding over the time scales of atmospheric response that affect its categorization as an ODS.

A simplified, yet realistic, model for CH$_3$Br and Br$^-$ has been analysed in terms of chemical modes and time scales (Prather 1997). Take a one-dimensional profile through the troposphere ($z=0$–14 km) and the stratosphere ($z=14$–52 km) with pressure $p(z)=10^{-z/16}$ atm and molecular density $N(z)=2.4\times10^{19} p(z)$ cm$^{-3}$. Transport is through vertical diffusion with rapid mixing in the troposphere ($K(z)=3\times10^5$ cm$^2$ s$^{-1}$ for 0–12 km) and a typical stratospheric diffusion profile ($K(z)=3\times10^3 p(14)/p(z)$ cm$^2$ s$^{-1}$ for 14–52 km). Photochemical loss of CH$_3$Br is assumed to occur at a constant frequency of $2.17\times10^{-8}$ s$^{-1}$ from 0 to 10 km and as $6\times10^{-12} p(z)^{-2}$ s$^{-1}$ above 10 km. For Br$^-$, assume that all CH$_3$Br loss equals Br$^-$ production and that the only loss of Br$^-$ is through rainout in the troposphere with a frequency of $2.315\times10^{-6}$ s$^{-1}$. These parameters are representative of the average values in the multidimensional atmospheric chemistry models.

With surface emissions of $90\times10^6$ kg yr$^{-1}$ of CH$_3$Br, a steady-state profile builds up with 10 ppt at the surface level as shown in figure 3 (solid line). The atmospheric burden is approximately $157\times10^6$ kg, and thus the steady-state lifetime is 1.75 yr. If all emissions cease, then the decay of CH$_3$Br from the atmosphere develops a prominent nose, with an e-fold time of 2.10 yr (dashed lines in figure 2). Where do this pattern and time scale come from?

In this case, the chemistry is linear and fixed and, ignoring Br$^-$ for now, there is only one species. Thus, the coupled chemical modes arise only through the transport operator in the continuity equation. The continuum in $z$ has been discretized by solving for CH$_3$Br at 14 grid points: $z_i=0, 4, 8, 12, 16, 20, \ldots, 48, 52$ km. A set of 14 continuity equations are entirely linear, using second-order finite-difference (diffusion) equations at interior points to couple the nearest neighbours and second-order flux boundary conditions at $z=0$ and 52 km. With appropriately normalized flux boundary conditions, the Jacobian derived from the continuity equation at each level $z_i$ is a 14×14 tridiagonal matrix with units of inverse time. If Br$^-$ is included, then the Jacobian is 28×28 and block tridiagonal with 2×2 blocks. In either case, it is easily solved for all eigenvalues and eigenvectors. Since there is no chemical feedback of Br$^-$ on CH$_3$Br in this system, the 14 eigenvalues/vectors of the 14×14 CH$_3$Br system are unchanged in the 28×28 matrix.

The 14 eigenvectors for the CH$_3$Br system are shown in figure 4 and labelled with their time constants. Most of the modes are short-lived, contain alternate signs (zero net mass) and represent mass-conserving diffusive exchange between the neighbouring points. The second longest-lived mode (1.34 yr) appears to be
an exchange between the troposphere and the stratosphere. The longest-lived mode (2.10 yr) matches the pattern and time scale of the long-term decay seen in figure 3. The 10 ppt CH$_3$Br in the $z=0$ level consists of 4.8 ppt e-folding at 2.10 yr, 5.0 ppt at 1.34 yr, 0.1 ppt at 0.02 yr and a small amount of the other 11 modes. Thus, the decomposition into modes allows analytical prediction of long-term behaviour equivalent to the numerical integration of the continuity equation and, further, helps identify the time scales and patterns of transport between reservoirs.

6. Time scales for nitrous oxide: radiative coupling through ozone

Nitrous oxide (N$_2$O), a greenhouse gas, is also a dominant source of stratospheric nitrogen oxides ($\text{NO}_Y=\text{NO}+\text{NO}_2+\text{HNO}_3+\text{N}_2\text{O}_5+\cdots$), which catalytically destroy O$_3$. The currently observed increase in N$_2$O is consistent with an increasing emission source from the agricultural use of nitrogen, poses a threat to the ozone layer and contributes to global warming. Analysis of a linearized one-dimensional troposphere–stratosphere model of the N$_2$O–$\text{NO}_Y$–O$_3$ system in terms of chemical modes (Prather 1998) shows how the radiative coupling through O$_3$ shortens the time for atmospheric decay of N$_2$O perturbations.

In the stratosphere, N$_2$O is destroyed by direct photolysis and reaction with meta-stable O($^1\text{D}$). Both reactions are controlled by O$_3$: locally, photolysis of O$_3$ is the source of O($^1\text{D}$); and globally, O$_3$ absorbs ultraviolet sunlight, thus limiting the photolysis rates. Stratospheric NO$_Y$ is produced by the reaction of O($^1\text{D}$)

Figure 3. Profile (solid line) of CH$_3$Br mixing ratio (ppt) versus altitude (km) at steady state driven by surface emissions. Also shown are the successive profiles (dashed lines) for years 1, 2, 4, 6 and 8 following cut-off of CH$_3$Br emissions. Initial loss of CH$_3$Br occurs at a rate (1.75 yr)$^{-1}$ given by the steady-state lifetime, but slows in a few years to that of the longest-lived mode time (2.10 yr)$^{-1}$ with the pattern of that mode (figure 4).
with N₂O and destroyed by washout in the troposphere and photolytic loss above 40 km. NO₃ enhances photochemical destruction of O₃. Thus, even locally, the N₂O–NO₃–O₃ system is a fully coupled chemical system, like the CH₄–CO–OH system. A simple model includes vertical diffusion between the stratosphere and the troposphere as for CH₃Br above, assumes rapid removal of NO₃ and O₃ below 10 km and linearizes stratospheric photochemistry in terms of the three variables (N₂O, NO₃ and O₃) about typical atmospheric conditions. The continuity equations can be solved for the steady state forced by an emission source of N₂O in the surface level (figure 5a).

Figure 4. Complete set of 14 chemical modes (eigenvectors) for the one-dimensional CH₃Br diffusion model (see text) in the order of increasing mode time (yr) shown above each. Eigenvectors are normalized to an absolute maximum of +1.

with N₂O and destroyed by washout in the troposphere and photolytic loss above 40 km. NO₃ enhances photochemical destruction of O₃. Thus, even locally, the N₂O–NO₃–O₃ system is a fully coupled chemical system, like the CH₄–CO–OH system. A simple model includes vertical diffusion between the stratosphere and the troposphere as for CH₃Br above, assumes rapid removal of NO₃ and O₃ below 10 km and linearizes stratospheric photochemistry in terms of the three variables (N₂O, NO₃ and O₃) about typical atmospheric conditions. The continuity equations can be solved for the steady state forced by an emission source of N₂O in the surface level (figure 5a). The Jacobian becomes a 42×42 block tridiagonal matrix with 3×3 blocks at each of the 14 vertical levels (for details, see Prather 1998). Chemical coupling is local and occurs through the 3×3 blocks along the diagonal. Transport coupling is between the neighbouring levels and is represented by the off-diagonal blocks. Since the abundance of O₃ in any layer affects the absorption and scattering of ultraviolet sunlight, and hence the photolysis rates in all layers, the radiative coupling is across all levels. Thus, the Jacobian is a sparse, but full matrix, which can nevertheless be readily solved for the chemical modes.

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Without the radiative coupling, the longest-lived mode has a mode time \( T_1 = 125 \text{ yr} \), close to the steady-state lifetime from the surface-level emissions, \( T_{SS} = 127 \text{ yr} \). The pattern of this mode shows uniform perturbations in \( \text{N}_2\text{O} \) and similar perturbations in \( \text{NO}_Y \) with half the relative amplitude. In \( \text{O}_3 \), the model produces a smaller relative depletion (opposite sign) centred about 32 km, where \( \text{NO}_Y \)-catalysed ozone destruction has its largest impact. The similarity of these two time scales almost justifies the use of \( T_{SS} \) as the e-folding time for \( \text{N}_2\text{O} \) emissions that is used in GWP and ODP calculations (e.g. Solomon et al. 1992). With radiative coupling, however, \( T_1 \) drops to 110 yr, the profile of the \( \text{N}_2\text{O} \) perturbation changes slightly, the \( \text{NO}_Y \) perturbation almost doubles and the \( \text{O}_3 \) self-healing effect gives positive perturbations in the lower stratosphere. Unlike the tropospheric \( \text{CH}_4\text{–CO–OH} \) system, the \( \text{N}_2\text{O}–\text{NO}_Y–\text{O}_3 \) system has negative feedbacks: increasing \( \text{N}_2\text{O} \) reduces \( \text{O}_3 \) in the middle stratosphere, allowing solar ultraviolet to destroy \( \text{N}_2\text{O} \) more rapidly.

Having solved for all 42 eigenvectors, we can readily analyse perturbations. Three patterns of \( \text{N}_2\text{O} \) perturbation are decomposed into the chemical modes with the six longest time scales shown in Table 1. A perturbation of 1000 kg matching the surface-forced steady-state profile is almost entirely mapped onto mode 1 (110-yr e-fold), but 1000 kg put entirely into the surface level (effectively 0–1 km) has 1025 kg in mode 1 with the balance made up of both positive and negative amounts in the short-lived modes. As expected, placing 1000 kg at 40 km has a much smaller impact on the long-term burden of \( \text{N}_2\text{O} \) with only 22 kg in mode 1,
and most of the 1000 kg going into short-lived modes (not shown), giving a steady-state lifetime for N2O of about 3 yr! A large ozone perturbation of $K_{10}$ Dobson units (approx. 3% of the total column), such as might result from a very large solar proton event, mostly recovers within weeks, but leaves behind a century-long deficit of 20 kg N2O in mode 1 (as summarized in table 1).

After this analysis, several multidimensional full chemistry models (Prather et al. 2001) examined the decay of an N2O perturbation and confirmed that the perturbation e-fold time was on average 8% less than the surface-emission steady-state lifetime.

### Table 1. Decomposition of a perturbation into kilogram (N2O) in the first six modes of the N2O–NO–O3 system.

<table>
<thead>
<tr>
<th>perturbation</th>
<th>mode (yr)</th>
<th>110</th>
<th>3.1</th>
<th>2.0</th>
<th>0.68</th>
<th>0.66</th>
<th>0.60</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 kg N2O at SS$^a$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 kg N2O at 0 km</td>
<td></td>
<td>999.5</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1000 kg N2O at 40 km</td>
<td></td>
<td>1025</td>
<td>2</td>
<td>−34</td>
<td>−2</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>−10 DU of O3 &gt; 28 km</td>
<td></td>
<td>−20</td>
<td>−17</td>
<td>0</td>
<td>−10</td>
<td>0</td>
<td>−8</td>
</tr>
</tbody>
</table>

$^a$Steady state as forced by continuous emissions at 0 km.

and most of the 1000 kg going into short-lived modes (not shown), giving a steady-state lifetime for N2O of about 3 yr! A large ozone perturbation of $K_{10}$ Dobson units (approx. 3% of the total column), such as might result from a very large solar proton event, mostly recovers within weeks, but leaves behind a century-long deficit of 20 kg N2O in mode 1 (as summarized in table 1).

After this analysis, several multidimensional full chemistry models (Prather et al. 2001) examined the decay of an N2O perturbation and confirmed that the perturbation e-fold time was on average 8% less than the surface-emission steady-state lifetime.

### 7. Integrating over environmental impacts: the magic of steady state

The steady-state pattern of trace species for specified emissions can be readily calculated using the chemical modes. Following the notation of §2, consider a perturbation, $\delta V_{SS}(x, y, z, n)$, that is the steady-state response to regular periodic emissions of trace species $(n)$. One can treat emission sources as the addition of trace species $(n)$ to specific $(x, y, z)$ locations or equivalently as a source pattern $S(x, y, z, n)$, which can be decomposed into the dimensionless eigenvectors (modes) $E_i$ with coefficients $b_i$, $S = \sum_{i=1:m} b_i E_i$. An infinitesimal amount of emissions, $Sdt$ (kg), from time $t$ in the past would have decayed according to each mode time, $\sum_{i=1:m} b_i E_i \exp(-t/T_i) dt$. The steady-state perturbation is, by definition, the integral of $Sdt$ from minus infinity to the present,

$$\delta V_{SS} = \int_{-\infty}^{0} Sdt = \sum_{i=1:m} b_i E_i \left( \int_{-\infty}^{0} \exp(-t/T_i) dt \right) = \sum_{i=1:m} T_i b_i E_i.$$

Assume that the source pattern $S$ comprises only emissions of species $(n)$, but allow for the perturbation $\delta V_{SS}$ to include all species $(n')$. The mass operator $M^n$, defined in §2, computes the global emissions rate (kg yr$^{-1}$) of species $(n)$ in the source pattern, $M^n[S] = \sum_{i=1:m} b_i m_i^n$ (kg yr$^{-1}$), and also the global burden (kg) in the steady-state perturbation, $M^n[\delta V_{SS}] = \sum_{i=1:m} T_i b_i m_i^n$ (kg), where $m_i^n = M^n[E_i]$ is dimensionless. Thus, the steady-state lifetime of species $(n)$ depends on the source pattern $S$ through the coefficients $b_i$:

$$T_{SS}(n) \equiv \frac{M^n[\delta V_{SS}]}{M^n[S]} = \frac{\sum_{i=1:m} T_i b_i m_i^n}{\sum_{i=1:m} b_i m_i^n} \text{ (yr)}.$$
A critical quantity in evaluating the overall environmental impact of a trace gas, such as the ODP or global warming potential, is the integrated abundance of the gas following a brief emission pulse. This integral needs to include not only the decay of the primary source gas, but also the accumulation and decay of any secondary products that impact radiative forcing or ODP. Thus, the general form will be the integrated change in species \( n' \) at some location \((x', y', z')\) following the initial perturbation represented by an emission pattern \( S(x, y, z, n) \) over a brief period \( \Delta \). For a short pulse of emissions, \( S(\Delta) \) (kg), the atmospheric perturbation \( \delta[V_\Delta(t)] = \sum_{i=1:m} \Delta b_i E_i \exp(-t/T_i) \) can be integrated forward in time to give the integrated impact, \( II \) (kg-yr),

\[
II(S\Delta) = \int_{t=0}^{\infty} \delta V_\Delta(t) dt = \Delta \sum_{i=1}^{m} T_i b_i E_i(x, y, z, n') = \Delta \delta V_{SS}(x, y, z, n').
\]

It can be rewritten using the definition of \( T_{SS}(n) \) as

\[
II(S\Delta) = \delta V_{SS}(x, y, z, n') T_{SS}(n) \left( \frac{M^n[S\Delta]}{M^n[\delta V_{SS}]} \right).
\]

Thus, the overall integrated perturbation caused by emission of a trace gas, including all secondary impacts, is given exactly by the steady-state pattern in all species multiplied by the steady-state lifetime of species \( n \) and then scaled by the ratio of the amount of \( n \) in the pulse to that in the steady-state pattern.

As an example, consider the ODP in response to the release of CH\(_3\)Br at the surface. The ozone depletion can be approximated by the perturbation to Br\(_Y\) at 20 km as shown in figure 6. There is a delay in the impact, as CH\(_3\)Br is transported into the stratosphere and is chemically converted into Br\(_Y\) (dark grey solid line). A peak in Br\(_Y\) is reached \( ca \) 6 yr following the release and is followed by a slow decay with the mode time of 4.52 yr, corresponding to the removal of a conservative tracer from the stratosphere. In this case, the release (kg) is scaled to be the amount of CH\(_3\)Br present in the atmosphere for a steady-state distribution forced by surface emissions resulting in 1 ppt at the surface. The area under the Br\(_Y\) curve is 0.73 ppt-yr. As shown above, this integral is exactly equal to the product of the steady-state lifetime for CH\(_3\)Br with surface emissions (1.75 yr) and the steady-state abundance of Br\(_Y\) at 20 km (0.42 ppt). It is almost universally assumed in assessments of ODP or climate forcing (Solomon et al. 1992; WMO 1995; IPCC 1996) that this integral is represented by a single e-fold decay of 1.75 yr (light grey solid line). Fortunately, the integrated impact is correctly evaluated with this assumption, but the time scale is not. Even with a 2.5-yr delay to allow for CH\(_3\)Br to reach the stratosphere (dashed line), the time scale of the response is incorrect (see Ko et al. 1997 for discussion). This mistaken view of time scales has led to the false reasoning in Montreal Protocol negotiations that reductions in CH\(_3\)Br would provide recovery of ozone within a few years: they do not.

The theory developed here applies readily to very short lived species, such as 1-C\(_3\)H\(_7\)Br, with a tropospheric residence time of weeks (Bridgeman et al. 2000; Olsen et al. 2000, Wuebbles et al. 2001). It provides a formal basis for computing the environmental impact using the readily calculated annual steady-state pattern of impacts (e.g. Br\(_Y\)) scaled by the annual steady-state lifetime of the source gas.
A concern with the simplified stratosphere–troposphere model used here is that the results are specific to the discrete finite grid used to solve the continuous diffusion equation. To test this, we experiment with the one-dimensional diffusion model, assuming zero flux at the top and a rapid loss (0.01 s\(^{-1}\)) only in the surface layer. Such a model should describe the stratospheric decay of a perturbation to a conserved species like Br\(_Y\), Cl\(_Y\), or SF\(_6\). (Note that decay is more rapid for a species like NO\(_Y\) with loss in the upper stratosphere.) The existence of distinct chemistry–transport modes is found even for the limiting case of a continuous semi-infinite atmosphere.

With the top at 52 km, increasing the vertical resolution from 4 to 1/4 km increases the number of eigenvalues in the one-dimensional troposphere–stratosphere model from 14 to 224. The evolutions of the four longest mode times (the smallest absolute eigenvalues) are shown in figure 7. Although all four mode times decrease by approximately 25% as the resolution increases, they remain separated and unique. Convergence of the values is apparent, and the difference between mode times on a grid size of 1 km and those in the continuous limit is approximately 10%.

8. Distinct modes: the infinite continuum

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Figure 6. Temporal behaviour of Br\(_Y\) (ppt) at 20 km in response to a single release of CH\(_3\)Br in the lowest level (0–1 km). The total release of CH\(_3\)Br (kg) is equivalent to the amount in a steady-state pattern from surface emissions (\(T_{SS} = 1.75\) yr) that maintain 1 ppt at the surface and also 0.417 ppt of Br\(_Y\) at 20 km. It is usually assumed that the Br\(_Y\) response to the CH\(_3\)Br release is represented by the steady-state level of Br\(_Y\) decaying with the e-fold time of \(T_{SS}\) (dark grey solid line): Br\(_Y\)(\(t\)) = 0.417 \(e^{-t/1.75}\). Sometimes a lag of 2.5 yr is adopted to approximate the delay in transport from troposphere to stratosphere (thin dashed line). The integrated area under this curve represents the cumulative environmental impact (e.g. on ozone depletion) of 0.73 ppt-yr. Neither case resembles the true rise and fall of Br\(_Y\) at 20 km following the release of CH\(_3\)Br (dark grey solid line): Br\(_Y\)(\(t\)) = 0.588 \(e^{-t/1.52}\) − 1.847 \(e^{-t/2.10}\) + 1.853 \(e^{-t/1.34}\) − 0.594 \(e^{-t/0.89}\) − 0.147 \(e^{-t/0.49}\) + 0.191 \(e^{-t/0.38}\) − 0.084 \(e^{-t/0.24}\) + 0.040 \(e^{-t/0.21}\). This curve can be simply integrated from the individual exponential terms (although some give a seemingly non-sensical negative impact) to give 0.73 ppt-yr, the same integral value as the steady-state e-fold but with a delayed impact.

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Providing a solution for the modes on a semi-infinite atmosphere poses a different problem. With an infinite upper boundary and constant diffusion coefficient $K$, Waugh & Hall (2002, reaction 9) show that the Green’s function used for age of air has an analytical form that precludes the simple exponential decay of the eigenvalue decomposition. In the stratosphere, typical profiles for $K$ have it increasing as density $N$ decreases (Ehhalt et al. 2004), and thus far we have chosen $K/N \approx 1$. In this test, three cases are chosen near the Waugh and Hall limiting form: (i) $K/N \approx 0.05$, (ii) $K/N \approx 0.01$, and (iii) $K/\text{constant}$. Leaving the grid step at 4 km, the one-dimensional model top is increased from 68 to 828 km (18 to 208 modes), and the evolution of the four longest mode times for each case is shown in figure 8. For case (i), the four solid lines show increasing mode times until the top reaches 200 km, with no change thereafter. For more slowly increasing $K$, case (ii), the four dashed lines show similar behaviour although the second through fourth longest mode times are still shifting even when the top reaches 828 km. For the previous examples with $K/N \approx 1$, the four longest mode times have converged to within 1% when the model top reaches 68 km. For case (iii), however, raising the upper boundary indeed changes the character of the chemistry–transport modes (dotted lines), and we approach a continuum of long-lived modes as anticipated.

9. The stratospheric decay mode: observed age of air, tritium and chlorine

The age of air in the stratosphere is defined as the time since the air was last in the troposphere, and the mean age can be directly observed with quasi-conserved trace gases that are increasing at a regular rate (e.g. CO$_2$, SF$_6$). In models, the
age of air can be calculated as a spectrum of ages from which the mean age can be evaluated (Waugh & Hall 2002). The mean age is related to the chemical modes. Specifically, the tail end of the spectrum corresponds to the mode describing stratospheric decay of a conserved tracer (see discussion above and Hall et al. 1999). The observed decay of stratospheric tritium ($^3$H) injected by atmospheric nuclear tests in the 1960s looks like a chemical mode (Ehhalt et al. 2004). The lag in recovery of upper stratospheric HCl following the decline of tropospheric HCl...
chlorofluorocarbons and other halocarbons in the 1990s is also a measure of the age of air spectrum and the long-lived modes (see discussion in Waugh & Hall 2002). Together, these observations provide the only current observational test of chemical modes.

A clear demonstration of the stratospheric decay mode was found with the Models and Measurements II project (Hall et al. 1999). For each model used to compute the age-of-air spectra, the original request had been to integrate 10–20 yr to ensure that the tail of the spectrum was well defined. Recognition that this tail represented the decay mode and that for each model it followed the same exact e-fold time throughout the stratosphere, however, enabled substantial savings in computation and a far easier evaluation of the mean age only after 6–10 yr of integration. In addition, Hall et al. (1999) and Ehhalt et al. (2004) showed that for all but one of the three-dimensional models, there was a simple linear relationship between the mean age at 30 km and the decay mode’s e-fold time.

Several years after injection, the decay of stratospheric tritium (as water above 20 km) followed a single exponential decay from 1969 to 1984. When corrected for the radioactive decay of tritium, this gives a decay mode time of \(7.7 \pm 2\) yr (Ehhalt et al. 2004). Allowing for a trend in stratospheric water that is consistent with the limited measurements, this decay mode time drops to 6.9 years. Corresponding mode times derived from the observed mean age range from 3.8 to 5.3 yr. Given the uncertainties associated with both of these derivations, a mode time between 5 and 6 yr is probable. Unfortunately, these values are still outside the range of decay mode times for all but one of the three-dimensional models, i.e. 1.44–4.75 yr (see table 2 of Ehhalt et al. 2004).

10. Chemistry–transport modes: three-dimensional tropospheric chemistry

In realistic simulations of global atmospheric chemistry with a three-dimensional chemistry–transport model (CTM), the continuity equation operators (Chem, Trans and Rad) change every hour or so. Presuming that this change is cyclic (e.g. the 24 h cycle of photolysis rates, the seasonal cycles of meteorological transport), the chemical modes should still exist but include another dimension that describes the temporal behaviour of perturbations over the daily/yearly cycle; e.g. \(E_i(x, y, z, n, t)\). Indeed, the existence of the long-lived, seasonally varying, \(CH_4\)-like, tropospheric chemistry mode has been sought for and characterized in at least two CTMs (Wild & Prather 2000; Derwent et al. 2001). The stratospheric decay mode was identified after the fact in many CTMs through the age-of-air experiments (Hall et al. 1999).

The number of CTM modes with an annually repeating meteorology readily exceeds \(10^6\), precluding the complete chemical mode decomposition shown in §§3–8. The longest-lived mode, however, can still be characterized by following the decay of perturbations. Wild & Prather (2000) and Derwent et al. (2001) found the decadal tropospheric mode \((CH_4–CO–OH–NO_x\cdots)\) of their CTMs by tracking a perturbation run minus control run for a decade following several different perturbations to tropospheric chemistry. (These CTMs did not include feedbacks with stratospheric chemistry that would have excited the century-long stratospheric N\(_2\)O-like mode.)
In one numerical experiment, Wild et al. increased global CH$_4$ emissions by 20%. The resulting perturbations to the CH$_4$, CO, O$_3$ and NO$_x$ abundances simulated for Mace Head, Ireland are shown in Figure 9. During the perturbation year, abundances of CH$_4$, CO and O$_3$ rise, while that of NO$_x$ falls. After the perturbation to emissions ceases (year 1), there are rapid decays involving short-lived modes, but within a few years, the perturbation curves assume the regular pattern of a repeating annual cycle that decays over any 12-month period with an e-fold time of 14.2 yr. Wild et al. extracted the longest-lived mode from these experiments, and the zonal-mean, mid-tropospheric, latitude-by-season patterns of CH$_4$ and CO are shown in Figure 10. The modes are dimensionless and are scaled to an absolute abundance of a single species as one point in space and time. In this example, the mode has been scaled to have an annual mean CH$_4$ perturbation of 100 ppb. The e-fold has been removed to show the annually repeating patterns. The seasonal variation in the CH$_4$ perturbation, 98–102 ppb, is similar to that in CO, 1–3 ppb, but with opposite phase in both latitude and season. The large annual variations of the mode at mid-latitudes indicate the importance of seasonal photochemistry.

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Tropospheric chemistry in these CTMs has only one dominant long-lived mode. Once it has been characterized for a given atmospheric simulation, its properties can be used to extrapolate almost all perturbations based on that control simulation. (Long-lived gases such as CHF₂Cl that are present in very low abundances will also produce decadal modes, but with very small amplitudes.) Recognizing this, both Derwent et al. (2001) and Wild et al. (2001) studied a wide range of perturbations to short-lived species such as NOₓ. They calculated the long-term climate impacts from 4-yr CTM simulations by integrating the short-term changes in O₃ and then deriving the amplitude of the long-lived mode to explicitly integrate over the decadal changes in CH₄ and O₃.

11. Development and future directions

The chemical coupling between the stratosphere and the troposphere remains largely unexplored. Thus far, we have separately identified the CH₄-like tropospheric and N₂O-like stratospheric chemical modes. However, the CH₄-like mode will perturb stratospheric O₃ directly through reactions involving CH₄ and indirectly by increasing stratospheric H₂O. Changes in stratospheric O₃ will perturb N₂O and also tropospheric CH₄ chemistry through changing photolysis rates and OH. Lower-dimension models (e.g. §§3–9) may not accurately represent the stratosphere–troposphere coupling, but CTM studies of any chemical perturbation with an N₂O-like mode will need to integrate the perturbation-minus-control simulations for 50 yr or more to separate these two modes.

A practical breakthrough could be achieved if global atmospheric chemistry can be approximated by a finite Jacobian. For a reasonable number of degrees of freedom (e.g. 1000), the system can be solved for all eigenvectors. If such a matrix represented most of the important chemical modes, then it would provide an explicit model for following the response to perturbations to any...
atmospheric species at any location. The challenge here is defining the space–
time averaging kernels to reduce the dimensionality of the system while
preserving the major modes.

One practical concern is whether the long-lived modes remain identifiable over
the year-to-year variations in meteorology. Although different CTMs with
different meteorological fields produce similar modes for stratospheric decay or
tropospheric CH$_4$ chemistry, they are different enough to preclude ready
evaluation of long-term impacts. Work with a single CTM and successive
years of forecast meteorological fields is ongoing and should provide a
quantitative measure of how the excitation and decay of chemical modes depend
on meteorology. Similar questions arise regarding large year-to-year variations in
atmospheric composition, such as for years with extensive forest fires.

Moving beyond atmospheric chemistry, extension of this approach to Earth
system models could yield surprises. The coupling across different components of
the chemistry–climate system, such as atmospheric chemistry, carbon cycle,
marine biogeochemistry, aerosols and climate, may introduce new linkages and
alter our expectation of the time scales of anthropogenic climate perturbations.
Defining and computing these coupled chemistry–climate modes will be challenging.

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**References**

Bolin, B. & Rodhe, H. 1973 Note on concepts of age distribution and transit-time in natural


Derwent, R. G., Collins, W. J., Johnson, C. E. & Stevenson, D. S. 2001 Transient behaviour of


*Phil. Trans. R. Soc. A* (2007)


