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Time scales in atmospheric chemistry: Theory, GWPs for CH_4 and CO, and runaway growth

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Abstract. Atmospheric CH_4 perturbations, caused directly by CH_4 emissions or indirectly by those of CO are enhanced by chemical feedbacks. They can be diagnosed in terms of the natural modes of atmospheric chemistry that are general solutions of the continuity equations. Each mode is a pattern in the global distribution of all chemical species, and each has a single time-constant that accurately describes its exponential decay about a given atmospheric state. This mathematical theory extends earlier work and is general for 2-D and 3-D chemistry-transport models. A formal proof relates the steady-state distribution and its lifetime to the integral of the true time-dependent response (properly included in the recent IPCC assessment). Changes in CO are also known to perturb CH_4; however, the impact of CO emissions on climate has not been formally assessed in part because the short lifetime of CO (months) relative to that of CH_4 (decade) was believed to limit the integrated impact. Using the IPCC model studies, this theory predicts that adding 5 CO molecules to today's atmosphere is equivalent to adding 1 CH_4 molecule with the same decadal duration as direct CH_4 addition. Extrapolating these results, CH_4 sources would have to triple before runaway growth, wherein CH_4 emissions exceed the oxidizing capacity of the troposphere.

1. Introduction

The abundance of trace gases and aerosols in Earth's atmosphere can determine the habitability of the planet. Human activities have significantly altered the atmospheric cycles of most trace gases, leading to their rapid increase over the past century. Methane is a greenhouse gas whose growth since the pre-industrial era has been documented in ice-core bubbles and recently in atmospheric measurements (Etheridge et al., 1992; Steele et al., 1992). Certain human activities (e.g., raising cattle, growing rice, use of natural gas) lead to direct release of CH_4 into the atmosphere. A major goal of methane-related research is to identify and quantify these sources and then to predict how CH_4 and other trace gases are affected (Cicerone and Oremland, 1988). Increases in CH_4 directly enhance the trapping of terrestrial infrared radiation, but they also perturb tropospheric chemistry: make O_3 in the upper troposphere (another greenhouse gas), reduce hydroxyl radical (OH) concentrations, increase carbon monoxide (CO). CH_4 increases also reach into the stratosphere: raise stratospheric H_2O levels, interfere with CFC-induced ozone depletion, and thence alter the amount of solar ultraviolet driving tropospheric photochemistry. The most difficult problem of atmospheric chemistry today is evaluating the cumulative and collective environmental impacts of all such chemical feedback loops associated with a single action, i.e. emission of one gas at one location.

Theoretical studies have long noted unusual behavior when CH_4 or CO were perturbed in tropospheric chemistry models (Chameides et al., 1976). Sze (1977) found CO perturbations to last several decades even though the CO lifetime was only a few months. Later studies identified the OH-CH_4 feedback as causing greater-than-proportional increases in steady-state CH_4 concentrations (Isaksen and Hov, 1987), e.g., +10% in emission yields +15% in concentration. Fisher (1993) found that small CH_4 pulses had e-fold times greater than the lifetime as defined by the budget (abundance/loss), contrary to the view that the average loss frequency of large reservoirs (e.g., tropospheric CH_4) should represent a time scale for change (the turn-over time or lifetime; see Bolin and Rodhe, 1973; O'Neill et al., 1994). Eigenvalue analysis of a single-box {CH_4, CO, OH}-system (Prather, 1994) explains the Fisher conundrum and why the system time scales are not the individual turn-over times.

This paper develops a general mathematical theory of eigenvalue methods for atmospheric chemistry in Section 2 that applies generally to multi-dimensional chemistry and transport models. A formal relationship between the natural modes and a steady-state distribution and lifetime is derived. Section 3 re-examines the one-box {CH_4, CO, OH}-system of Prather (1994) with this formalism using multi-dimensional model studies to constrain the chemical feedbacks. IPCC's (1995) use of an "extended" lifetime to assess small CH_4 perturbations is shown to be rigorously correct; however, generation of long-lived, CH_4-like perturbations from CO and other short-lived gases, predicted here, has not yet been addressed. The degree of non-linearity as a function of CH_4 source is examined, as well as the potential for run-away CH_4 growth. Section 4 summarizes the advantages of diagnosing action-and-effect in terms of natural modes.

2. Eigenvalue Theory - Atmospheric Chemistry

The continuity equation (1) for the concentration of each atmospheric species at a given spatial location, x_k, can be expressed in terms of its local net chemical production, p_k, and its transport tendency, $\nabla\phi_k$, a flux divergence. These individual equations can be written as a single vector equation (2), X being a vector of species concentrations x_k where $k=i+m(j-1)$, i = 1:m is the species index and j = 1:n is the spatial location. The vector P represents the individual p_k, (function of different species at the same location); and the vector $\nabla\Phi$, the individual $\nabla\phi_k$ (like species at neighboring locations). The nmxnm Jacobian matrix **J** is defined (3) as the partial derivative of each equation (1) with respect to

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each independent variable, x_k. Let the vector of chemical species $X^o(t)$ be a time-dependent solution to (2), then solve for a perturbation, $X^o + D$, by expanding equation (2) in a Taylor series (4). Only the chemical terms are non-linear and appear in (4) as second-order terms. To first-order, the perturbation vector D satisfies the matrix equation (5). If a perturbation A^k is an eigenvector of **J** with eigenvalue $-c_k$, then the vector solution to (5) decays, maintaining its pattern, as a simple exponential (6).

The natural modes in atmospheric chemistry are the eigenvectors A^k (k=1:nm) whose set spans the nm-dimensional space of chemical species. Any perturbation D has a unique expansion with coefficients d_k and decays with an ensemble of decay frequencies corresponding to the eigenvalues (7). These modes are basic properties of the atmospheric state, not of the perturbation. The vectors A^k are independent of the perturbation D provided that the Jacobian varies slowly: $\mathbf{J}[X^o+D] \approx \mathbf{J}[X^o]$, meaning the terms of order D^2 in (4) are negligible. In a fully linear system **J** is constant, and any state, not just a small perturbation, is described by natural modes (7). A real, asymmetric matrix like **J** can have positive, negative, or complex eigenvalues. Provided that all eigenvalues are negative ($-c < 0$), any perturbation decays. If there were a single positive eigenvalue of $\mathbf{J}[X^o]$, then the system would be locally unstable about X^o since any realistic perturbation would likely excite the unstable eigenvector. Although complex eigenvalues in atmospheric chemical systems are rare, such oscillating "clocks" are known (Nitzan and Ross, 1973).

$$dx_k/dt = p_k - \nabla\phi_k \tag{1}$$

$$dX/dt = P - \nabla\Phi \tag{2}$$

$$\mathbf{J}_{ik} \equiv \partial(dX/dt)_i / \partial x_k = \partial(P)_i/\partial x_k - \partial(\nabla\Phi)_i/\partial x_k \tag{3}$$

$$\begin{aligned} d(X^o(t)+D)_i/dt &= (P[X^o(t)+D] - \nabla\Phi[X^o(t)+D])_i \qquad (4)\\ &= (P[X^o(t)] - \nabla\Phi[X^o(t)])_i + \Sigma_{k=1:nm}\{\partial(P)_i/\partial x_k \\ &\quad - \partial(\nabla\Phi)_i/\partial x_k\}(D)_k + \mathrm{Order}(\partial^2P/\partial X^2\ D^2) \\ &= d(X^o(t))_i/dt + \Sigma_{k=1:nm}\mathbf{J}_{ik}(D)_k + \mathrm{Order}(\partial^2P/\partial X^2\ D^2) \end{aligned}$$

$$dD/dt = \mathbf{J}\ D \tag{5}$$

$$dA^k/dt = -c_k\ A^k \Rightarrow A^k(t) = A^k(0)\ \exp[-c_kt] \tag{6}$$

$$D(0) = \Sigma_{k=1:nm}d_kA^k \Rightarrow D(t) = \Sigma_{k=1:nm}d_kA^k\ \exp[-c_kt] \tag{7}$$

A steady-state distribution and its lifetime can be related to the natural modes. Continuous forcing of the system at the same rate over an infinite time (i.e., integrating (2)) builds up a steady-state distribution SS(z), where the spatial variable z is explicitly noted. Consider the natural modes $A^k(z)$ of a single-species system (m=1) where each mode is a spatial pattern (with n degrees of freedom). The rate of emission of a gas (kg/sec) integrated over a brief period (1 sec) produces a spatial pattern of abundance F(z) (kg), which maps onto the natural modes (8) (e.g., surface emissions place a certain amount in the lowest layer). The modes A^k are dimensionless, and the coefficients f_k have units of abundance (kg). The individual modes represented in each burst of emissions, F(z), decay according to their eigenvalue frequencies c_k. The steady-state distribution (kg) is comprised of an infinite history of emissions, F(z,t), from all previous times (9). The normalization factor, u (=1 sec here), converts the sum to an integral. The steady-state lifetime T_{SS} is the total burden (kg) divided by emissions (or loss rate, kg/s), and can be derived (10), recognizing that the steady state is a mix of modes (9) each with its own loss frequency. It is simply the sum of the lifetimes of the individual modes, $1/c_k$, weighted by the abundance in that mode, f_ka_k, where $a_k \equiv \int A^k(z)dz$ (10). T_{SS} is often mistakenly assumed to be a fundamental time constant of the system; whereas, the true system time scales for perturbations are the inverse eigenvalues of the Jacobian.

The net environmental impact, I, of trace-gas emissions is measured by integrating over the resulting atmospheric perturbations (e.g., kg-sec or ppt-yr). This integral is usually assumed (IPCC, 1995; WMO, 1995) to be the product of the steady-state distribution and the corresponding mean lifetime, viz $I(z) \approx SS(z)\ T_{SS}$. Using natural-mode decomposition, the cumulative impact of a scaled pulse, s F(z), is calculated by explicit integration (11) and can be related to a steady-state distribution with the same global content by selecting the appropriate scale factor, s, (12). Thus equations (9-12) prove that the IPCC/WMO assumption is exact ($I[sF(z)] \equiv SS(z)\ T_{SS}$), that the sum of the integrals of the exponentially decaying modes is exactly represented by the product of the steady-state lifetime and its distribution, even though T_{SS} may not describe the recovery time scale. (N.B. Due to non-linear chemistry, T_{SS} for a CH_4 perturbation, 15.4 yr, is not the same as the CH_4 budget lifetime, 9.6 yr, see Section 3).

The longer-lived modes (i.e., smaller absolute eigenvalues) contribute most to the steady-state distribution (see 9) and are of most interest in following the decay of a perturbation. As spatial resolution increases, new modes appear for each new degree of freedom. However, these will have short time scales, usually corresponding to nearest-neighbor transport or rapid local chemistry (e.g., OH). The primary and other long-lived chemical-transport modes should change little. Because the modes are not orthogonal, representing a perturbation, S, as a combination of modes, $\Sigma_{k=1:nm}s_kA^k$, requires the complete set of modes, the matrix **A**, to solve for the coefficients of each mode, $s_k = (\mathbf{A}^{-1}S)_k$. The modes for 1-D models (nm≈100) can be calculated directly and completely; however, for more realistic 2-D and 3-D models with many chemicals (nm>10^6), calculation of the modes will need a different approach. The long-lived modes may be found numerically by following out the tail of a perturbation and fitting it to a sum of exponential decays; and some information about the matrix **A** may be found by noting how different perturbations excite these principal modes.

$$F(z) = \Sigma_{k=1:n}\ f_k\ A^k(z) \tag{8}$$

$$\begin{aligned} SS(z) &= \Sigma_{t=-\infty:0}\ F(z,t) \qquad (9)\\ &= \Sigma_{t=-\infty:0}\ \{\Sigma_{k=1:n}\ f_k\ A^k(z)\ \exp[-c_kt]\} \\ &= \Sigma_{k=1:n}\ f_k\ A^k(z)\ \{\textstyle\int_{-\infty}^{0} \exp[-c_kt]\ dt/u\} \\ &= \Sigma_{k=1:n}\ (f_k/c_ku)\ A^k(z) \end{aligned}$$

$$\begin{aligned} T_{SS} &= \{\textstyle\int SS(z)dz\} \,/\, \{\Sigma_{k=1:n}\ c_k(f_k/c_ku)\textstyle\int A^k(z)dz\} \qquad (10)\\ &= \{\ \Sigma_{k=1:n}\ (1/c_k)\ f_ka_k\ \} \,/\, \{\ \Sigma_{k=1:n}\ f_ka_k\ \} \end{aligned}$$

$$\begin{aligned} I[s\ F(z)] &= s\ \Sigma_{k=1:n}\ f_k\ A^k(z) \textstyle\int_0^\infty \exp[-c_kt]dt \qquad (11)\\ &= s\ \Sigma_{k=1:n}\ f_k/c_k\ A^k(z) = s\ u\ SS(z) \end{aligned}$$

$$s \textstyle\int F(z)\ dz = \textstyle\int SS(z)\ dz \tag{12}$$

$$\Rightarrow s = \Sigma_{k=1:n}\ f_ka_k/(c_ku) \,/\, \Sigma_{k=1:n}\ f_ka_k$$

$$\Rightarrow s\ u = T_{SS}$$

3. Non-linearity in the {CH_4, CO, OH}-system

The chemical cycles of CH_4, CO, and OH in the global atmosphere are coupled (Levy, 1972). They also involve other species (e.g., NO, C_2H_6) and transport that connects different photochemical regimes (e.g., Isaksen and Hov, 1987; Cicerone and Oremland, 1988). Nevertheless, this system is usefully studied with a one-box model (Prather, 1994) as defined in Table 1. Here the rate coefficients, air density, and source terms are selected to constrain the one box to represent a "global mean": CH_4=1700 ppb, CO=100 ppb, CH_4 budget lifetime = 9.6 yr. The single remaining free variable is diagnosed from the CH_4 feedback factors, $R=1/(1-\delta \ln T_{CH4}/\delta \ln CH_4)$, reported by multi-dimensional models in IPCC (Prather et al., 1995). In this formalism, R = $-J_{11}/c_1$, the time scale of the primary mode divided by the lifetime of CH_4. In the one-box model, R sums up complexities not included such as the partial recycling of OH by ROO+NO reactions during oxidation of CH_4.

For typical feedbacks, R=1.6 (IPCC range 1.2-1.7), about 50% of OH production is lost to CH_4 and CO. The lifetimes of CH_4, CO, and OH are 9.6 yr, 88 d, and 0.71 s, respectively. The modes are linearly independent but not orthogonal; and thus an isolated perturbation to CH_4, CO, or OH becomes a unique mix of all three modes (see Table 1): 1000 CH_4 molecules become 993 CH_4 molecules in the primary CH_4-like mode (e-fold time of 15.5 yr), 7 molecules in the CO-like mode (e-fold time of 109 d), and only a fraction of a molecule in the OH-like mode (e-fold time of 0.71 s). The accumulation from a continuous source of 1 ppb/yr is 15.4 ppb, and thus the steady-state lifetime for CH_4 additions to today's atmosphere is 15.4 yr (Isaksen & Hov, 1987), differing slightly from that of the primary mode. This should not be confused with the 9.6-yr lifetime based on the total CH_4 budget. This 9.6-yr time scale is seen briefly in the initial decay of the CH_4 pulse when rapid decay of the small amount of CH_4 in the OH-like mode is included.

TABLE 1. The One-Box {CH_4, CO, OH} Model

Chemical Reactions (net):
1: $OH + CH_4 \Rightarrow CO + ...$
2: $OH + CO \Rightarrow ...$
3: $OH + X \Rightarrow ...$

Continuity Equations:
$d[CH_4]/dt = S_{CH4} - k_1[OH][CH_4]$
$d[CO]/dt = S_{CO} + k_1[OH][CH_4] - k_2[OH][CO]$
$d[OH]/dt = S_{OH} - k_1[OH][CH_4] - k_2[OH][CO] - k_3[OH][X]$

Constants: [air, 20°C] = 2.5×10^{19} cm^{-3}
$k_1=5.\times10^{-15} cm^3s^{-1}$ $k_2=2.\times10^{-13} cm^3s^{-1}$ $k_3[X]=0.7\ s^{-1}$
S_{CH4} = 177 ppb/yr S_{CO} = 240 ppb/yr S_{OH} = 1180 ppb/yr

Steady-State (d[_]/dt=0) solution:
$[CH_4]$ = 1700 ppb [CO] = 100 ppb [OH] = 6.6×10^5 cm^{-3}

Lifetimes or Turn-Over times ($-1/J_{ii}$):
$T_{SS}(CH_4)$ = 9.60 yr $T_{SS}(CO)$ = 88 d $T_{SS}(OH)$ = 0.71 s

Modes:	A^1	A^2	A^3
$-1/c_i$:	15.5 yr	109 d	0.71 s
CH_4:	1.000	-0.192	0.150
CO:	0.0385	1.000	0.204
OH:	-6.0e-9	-9.3e-9	1.000

Decomposition of $\Delta[CH_4]$=1 ppb into modes ($\sum a_i A^i \exp[-c_k t]$):
$0.9927\ e^{-t/15.5} + 0.0073\ e^{-t/0.30} + 3.5\times10^{-10}\ e^{-t/2E-8}$ ppb

Steady-State accumulation from ΔS_{CH4} = 1 ppb/yr ($\sum a_i A^i/c_i$):
$0.9927\times15.5 + 0.0073\times0.30 + 3.5\times10^{-10}\times2\times10^{-8} = 15.4$ ppb

Instantaneous (t=0) decay rate of $\Delta[CH_4]$=1 ppb ($\sum c_i a_i A^i$):
$d\Delta[CH_4]/dt = 0.0641 + 0.0244 + 0.0158 = 0.1043$ ppb yr^{-1}
= 1 ppb / 9.6 yr

Decomposition of $\Delta[CO]$=1 ppb into 1st & 2nd modes:
$\Delta[CO] = 0.007\ e^{-t/15.5} + 0.993\ e^{-t/0.30}$ ppb
$\Delta[CH_4] = 0.191\ e^{-t/15.5} - 0.191\ e^{-t/0.30}$ ppb

CH_4 feedback factors, $R=1/(c_i T_{SS})$, impact on 1st mode:

R=1.41	$1/c_1$= 13.6 yr	{$k_3[X]=1.05\ s^{-1}$; S_{OH}=1460ppb/yr}
R=1.61	$1/c_1$= 15.5 yr	{base case here}
R=2.73	$1/c_1$= 26.2 yr	{$k_3[X]=0.25\ s^{-1}$; S_{OH}=800 ppb/yr}

The coupling of CO perturbations to CH_4 is not new (Sze, 1977); however, the formalism of natural modes allows us to write explicitly the magnitude and time dependence of the coupling as given in Table 1. The addition of 1000 molecules of CO produces a mix of all three modes: 993 molecules of CO in the secondary 0.30-yr mode, 7 molecules in the primary 15.5-yr mode, and less than 1 molecule in the short-lived mode. The perturbations to CH_4 from this CO addition are off-setting at t=0 as expected: -191 (negative!) molecules of CH_4 in the secondary mode, and +191 molecules of CH_4 in the primary mode. The decay of the secondary mode produces a rapid rise (0.30 yr) in CH_4 and then leaves us with a long-term perturbation to CH_4 that is 19% as large (molecule-per-molecule) as the CO perturbation.

Methane concentrations have risen steadily from about 600 ppb since the pre-industrial era, are still rising, and may be caused in part by chemical coupling with other changes (e.g., Khalil et al., 1985; Levine et al., 1985; Thompson and Cicerone, 1986). CH_4 concentrations as a function of source are shown in Figure 1a for the three R values summarized in Table 1. Each case passes through the circle denoting today's conditions. For likely R (1.4-1.6, IPCC, 1995), the previous history of CH_4 is mainly linear; however, the future may be less so. A doubling of the current source is predicted to lower OH concentrations so much that CH_4 reaches 10,000 ppb, a factor-of-6 increase. If CH_4 sources treble, there is runaway growth, and no steady-state solution exists. In the case R=2.7 (unlikely from IPCC results), the change since pre-industrial is already non-linear, and the preindustrial source was more than half as large as that today. In this case, a runaway system occurs with only a 50% increase in today's CH_4 emissions. This instability needs to be re-examined with multi-dimensional models that couple varied photochemical regimes (tropics/poles, tropo/stratosphere).

The non-linearity of the {CH_4, CO, OH}-system becomes more severe at higher CH_4 concentrations. This change in the primary mode's time scale is shown in Figure 1b. For R=1.4-1.6 the time scale of the primary mode rises from 14-16 yr today to 22-29 yr at doubled CH_4 concentration. Also, the CO⇒CH_4 coupling, already a function of R (15-19% for R=1.4-1.6), becomes even greater at doubled CH_4 (22-27%, not shown). Thus CH_4 perturbations will become increasingly longer lived as its absolute abundance increases and its environmental impact (e.g., global warming potential, GWP) increases similarly. More accurate evaluation of the {CH_4, CO, OH}-coupling in today's atmosphere with multi-dimensional models is vital for predicting future composition and climate.

4. GWPs, ODPs, and Other Applications

A natural mode in atmospheric chemistry is a pattern: a co-variation of coupled chemicals including spatial and/or seasonal variations. Natural modes are the eigenvectors of the Jacobian matrix derived from linearizing the spatially discretized time-tendency equations for each chemical species. This application of eigenvalue techniques opens new oppor-

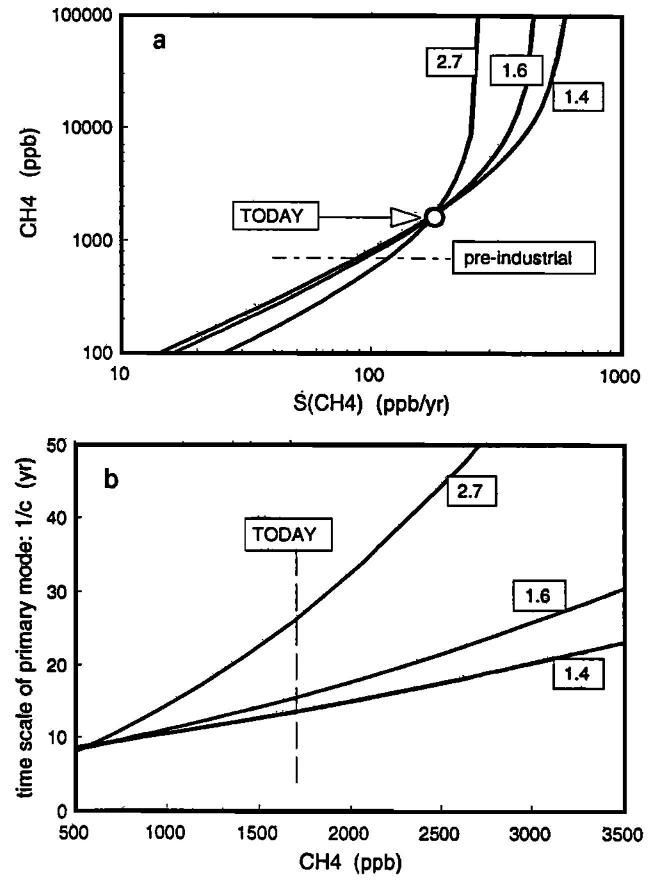

Figure 1. (a) Concentration of CH_4 (ppb) as a function of source $S(CH_4)$ (ppb/yr). Models are labeled by increasing levels of chemical feedback (R, see text). All models are constrained by today's concentration and lifetime (circle). Pre-industrial level is shown by the dashed line. For $S > 270$ ppb/yr, the R=2.7 case has no steady-state solution.
(b) Time scale of primary mode as a function of CH_4 concentration, labeled by R. This time scale increases more rapidly with CH_4 than does its lifetime (not shown).

tunities for studying coupled perturbations in atmospheric chemistry and presents new methods of diagnosing the increasingly complex 3-D chemical transport models.

(1) Natural modes are a mathematically rigorous, fundamental property of the chemical-transport system (i.e., current atmosphere) and do not depend on the perturbation. (2) Exponential decay of each natural mode with its own time scale is an exact solution in the linear limit. (3) A steady-state pattern and lifetime can be derived from the modes. (4) The integral of a pulsed source is identical to the corresponding steady-state's lifetime multiplied by its concentration. (5) True time scales in atmospheric chemistry (the e-fold times for the modes) are often different from the turn-over or lifetimes. (6) A unique mix of modes (effects) is excited by perturbations to a single species (cause).

Short-lived gases like CO have can affect indirectly the trends of other gases like CH_4 and tropospheric O_3 (e.g., Thompson and Cicerone, 1986). These "indirect" perturbations are shown here to have the same pattern and time scale as those caused by direct addition of the long-lived species. Although extremely difficult to evaluate with confidence, the emissions of very short-lived gases (e.g., CO, NO, C_2H_6) should be treated as having a long-term environmental impact and given an ODP (ozone depletion potential) or GWP in proportion to the amplitude of the induced long-lived natural modes. Individual perturbations couple across all modes of tropospheric and stratospheric chemistry. We can expect emissions of a short-lived gas such as CO (months) to lead to a long-lived perturbation in CH_4 (decade) as shown here and perhaps even a longer-lived perturbation in N_2O (century). Extension of this method to examples with transport (CH_3Br in the stratosphere, troposphere and ocean) and uv radiative coupling (N_2O, NO_y, and O_3 in the stratosphere) is presented in a following paper.

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