Title
Time scales in atmospheric chemistry: Theory, GWPs for CH4 and CO, and runaway growth

Permalink
https://escholarship.org/uc/item/3tx379vd

Journal
GEOPHYSICAL RESEARCH LETTERS, 23(19)

ISSN
0094-8276

Author
Prather, MJ

Publication Date
1996-09-15

DOI
10.1029/96GL02371

License
https://creativecommons.org/licenses/by/4.0/ 4.0

Peer reviewed
Time scales in atmospheric chemistry: Theory, GWPs for CH\textsubscript{4} and CO, and runaway growth

Michael J. Prather
Earth System Science, University of California at Irvine

Abstract. Atmospheric CH\textsubscript{4} perturbations, caused directly by CH\textsubscript{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 away from 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\textsubscript{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\textsubscript{4} (decade) was believed to limit the integrated impact. The IPCC model studies, this theory predicts that adding 5 CO molecules to today's atmosphere is equivalent to adding 1 CH\textsubscript{4} molecule with the same decadal duration as direct CH\textsubscript{4} addition. Extrapolating these results, CH\textsubscript{4} sources would have to triple before runaway growth, wherein CH\textsubscript{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\textsubscript{4} into the atmosphere. A major goal of methane-related research is to identify and quantify these sources and then to predict how CH\textsubscript{4} and other trace gases are affected (Cicerone and Oremland, 1988). Increases in CH\textsubscript{4} directly enhance the trapping of terrestrial infrared radiation, but they also perturb tropospheric chemistry: make O\textsubscript{3} in the upper troposphere (another greenhouse gas), reduce hydroxyl radical (OH) concentrations, increase carbon monoxide (CO). CH\textsubscript{4} increases also reach into the stratosphere: raise stratospheric H\textsubscript{2}O 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\textsubscript{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\textsubscript{4} feedback as causing greater-than-proportional increases in steady-state CH\textsubscript{4} concentrations (Isaksen and Hov, 1987), e.g., +10\% in emission yields +15\% in concentration. Fisher (1993) found that small CH\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{4} perturbations is shown to be rigorously correct; however, generation of long-lived, CH\textsubscript{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\textsubscript{4} source is examined, as well as the potential for run-away CH\textsubscript{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) \(\nabla X\) being a vector of species concentrations \(x_k\) where \(k'=1,m\) 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 \(n\times m\) Jacobian matrix \(J\) is defined (3) as the partial derivative of each equation (1) with respect to
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: \( J[X^o+D] = J[X^o] \), 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 eigenvalues that are negative (\( -c < 0 \)), any perturbation decays. If there were a single positive eigenvalue of \( J[X^o] \), 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 (Niztan and Ross, 1973).

\[
dx_i/dt = p_k - \nabla \Phi_k \tag{1}
\]

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

\[
J_{ik} = \partial (dx_i/dt)/\partial x_k = \partial (P)/\partial x_k - \partial (\nabla \Phi)/\partial x_k \tag{3}
\]

\[
d(X^o(t)+D)/dt = (P[X^o(t)+D] - \nabla \Phi[X^o(t)+D])_i = (P[X^o(t)] - \nabla \Phi[X^o(t)]_i + \sum_{k=1:nm} \partial (P)/\partial x_k \nabla \Phi [X^o(t)]_i - \partial (\nabla \Phi)/\partial x_k ) (D)_k + \text{Order}(\partial^2 P/\partial x^2 D^2) \tag{4}
\]

\[
dD/dt = J D \tag{5}
\]

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

\[
D(0) = \sum_{k=1:nm} d_k A^k \Rightarrow D(t) = \sum_{k=1:nm} d_k A^k \exp[-c_k t] \tag{7}
\]

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 model (\( m=1 \)) 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 \( d_k \) 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 see 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, \( f_k a_k \), where \( a_k = [A^k(z)dz] \) (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, \( \text{I}(z) = SS(z) T_{ss} \). 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 (\( \text{I}(sF(z)) = SS(z) T_{ss} \)), 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).
3. Non-linearity in the (CH₄, CO, OH) system

The chemical cycles of CH₄, CO, and OH in the global atmosphere are coupled (Levy, 1972). They also involve other species (e.g., NO, C₂H₄) 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 described in Table 1. Here the rate coefficients, air density, and source terms are selected to constrain the one box to represent a "global mean": CH₄=1700 ppb, CO=100 ppb, CH₄ budget lifetime ≈ 9.6 yr. The single remaining free variable is diagnosed from the CH₄ feedback factors, R=1/(1-S₄₄/6nT₄₄), reported with multi-dimensional models in IPCC (Prather et al., 1995). In this formalism, R = -J₁/c, the time scale of the primary mode divided by the lifetime of CH₄. 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 CH₄.

For typical feedbacks, R=1.6 (IPCC range 1.2-1.7), about 50% of OH production is lost to CH₄ and CO. The lifetimes of CH₄, CO, and OH are 9.6 yr, 88 d, and 0.71 s, respectively. The modes are linearly independent but not orthogonal; thus an isolated perturbation to CH₄, CO, or OH becomes a unique mix of all three modes (see Table 1): 1000 CH₄ molecules become 993 CH₄ molecules in the primary CH₄-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 CH₄ on the time scale of the primary mode divided by the lifetime of CH₄. 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 CH₄.

For typical feedbacks, R=1.6 (IPCC range 1.2-1.7), about 50% of OH production is lost to CH₄ and CO. The lifetimes of CH₄, CO, and OH are 9.6 yr, 88 d, and 0.71 s, respectively. The modes are linearly independent but not orthogonal; thus an isolated perturbation to CH₄, CO, or OH becomes a unique mix of all three modes (see Table 1): 1000 CH₄ molecules become 993 CH₄ molecules in the primary CH₄-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 CH₄ on the time scale of the primary mode divided by the lifetime of CH₄. 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 CH₄.

For typical feedbacks, R=1.6 (IPCC range 1.2-1.7), about 50% of OH production is lost to CH₄ and CO. The lifetimes of CH₄, CO, and OH are 9.6 yr, 88 d, and 0.71 s, respectively. The modes are linearly independent but not orthogonal; thus an isolated perturbation to CH₄, CO, or OH becomes a unique mix of all three modes (see Table 1): 1000 CH₄ molecules become 993 CH₄ molecules in the primary CH₄-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 CH₄ on the time scale of the primary mode divided by the lifetime of CH₄. 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 CH₄.
Although extremely difficult to evaluate with confidence, the current atmosphere and do not depend on the perturbation. Rapidly with CH$_4$ than does its lifetime (not shown). Constraints 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. Analysis Program and NSF's Atmospheric Chemistry Program for support of this research. This paper would not have been possible without Don Fisher's willingness to report his unusual results at the AFEAS workshop, without Detlev Huelsebusch's summer research project setting up the 1-D model, and without Ralph Cicerone's admonishments not to give up.

References

Bolin, B., and H. Rodhe, A note on the concepts of age distribution and transit time in natural reservoirs, Tellus, 25, 58-62, 1973.

Chameides, W.L., S.C. Liu, and R.J. Cicerone, Possible variations in atmospheric methane, J. Geophys. Res., 81, 4997-5001, 1976.

Cicerone, R.J. and R.S. Oremland, Biogeochemical aspects of atmospheric methane, Glob. Biogeochem. Cycles, 2, 299-327, 1988.

Etheridge, D.M., G.I. Pearman, and P.J. Fraser, Changes in tropospheric methane between 1841 and 1978 from a high accumulation-rate Antarctic ice core, Tellus, 44B, 282-294, 1992.

Fisher, D.A., paper presented at Workshop on the Atmospheric Degradation of HCFCs and HFCs, Boulder CO, Alternative Fluorocarbons Environmental Acceptability Study, eds. M.J. Kurylo, A.R. Ravishankara, A. McCulloch, 17-19 Nov 1993.

IPCC, Climate Change 1994, Intergovernmental Panel on Climate Change, J.T. Houghton et al., eds., Camb. U. Press, 339 pp., 1995.

Isaksen, I.S.A., and O. Hov, Calculation of trends in tropospheric $O_3$, OH, CH$_4$, & NO, Tellus, 39B, 271-285, 1987.

Khalil, M.A.K., and R.A. Rasmussen, Causes of increasing atmospheric methane: depletion of OH radicals and the rise of emissions, Atmos. Environ. 19 397-407, 1985.

Levine, J.S., C.P. Rinsland, and G.M. Tennyille, The photochemistry of methane and carbon monoxide in the troposphere in 1950 and 1985, Nature, 318, 254-257, 1985.

Levy, H., Photochemistry of the lower troposphere, Planet. Space Sci., 20, 919-935, 1972.

Nitzan, A. and J. Ross, Oscillations, multiple steady states and instabilities in illuminated systems, J. Chem. Phys. 59, 241-250, 1973.

O'Neill, B.C., S.R. Gaffin, F.N. Tubiello, and M. Oppenheimer, Reservoir timescales for anthropogenic CO$_2$ in the atmosphere, Tellus, 46B, 378-389, 1994.

Prather, M.J., Lifetimes and eigenstates in atmospheric chemistry, Geophys. Res. Lett., 21, 801-804, 1994.

Prather, M., R. Derwent, D. Ehhalt, G.I. Pearman, P.J. Fraser, and R. Derwent, D. Ehhalt, P. Fraser, E Sanhueza, X. Zhou. Chapter 2: Other tracer gases and atmospheric chemistry, in Climate Change 1994, IPCC, J.T. Houghton et al., eds., Cambridge U. Press, pp. 73-126, 1995.

Steele, L.P., E.J. Dlugokencky, P.M. Lang, P.P. Tans, R.C. Martin, and K.A. Masarie, Slowing down of the global accumulation of atmospheric methane: depletion of OH radicals and the rise of emissions, Atmos. Environ. 19 397-407, 1985.

Levy, H., Photochemistry of the lower troposphere, Planet. Space Sci., 20, 919-935, 1972.

Nitzan, A. and J. Ross, Oscillations, multiple steady states and instabilities in illuminated systems, J. Chem. Phys. 59, 241-250, 1973.

O'Neill, B.C., S.R. Gaffin, F.N. Tubiello, and M. Oppenheimer, Reservoir timescales for anthropogenic CO$_2$ in the atmosphere, Tellus, 46B, 378-389, 1994.

Prather, M.J., Lifetimes and eigenstates in atmospheric chemistry, Geophys. Res. Lett., 21, 801-804, 1994.

Prather, M., R. Derwent, D. Ehhalt, G.I. Pearman, P.J. Fraser, and R. Derwent, D. Ehhalt, P. Fraser, E Sanhueza, X. Zhou. Chapter 2: Other tracer gases and atmospheric chemistry, in Climate Change 1994, IPCC, J.T. Houghton et al., eds., Cambridge U. Press, pp. 73-126, 1995.

Steele, L.P., E.J. Dlugokencky, P.M. Lang, P.P. Tans, R.C. Martin, and K.A. Masarie, Slowing down of the global accumulation of atmospheric methane: depletion of OH radicals and the rise of emissions, Atmos. Environ. 19 397-407, 1985.

Levy, H., Photochemistry of the lower troposphere, Planet. Space Sci., 20, 919-935, 1972.

Nitzan, A. and J. Ross, Oscillations, multiple steady states and instabilities in illuminated systems, J. Chem. Phys. 59, 241-250, 1973.

O'Neill, B.C., S.R. Gaffin, F.N. Tubiello, and M. Oppenheimer, Reservoir timescales for anthropogenic CO$_2$ in the atmosphere, Tellus, 46B, 378-389, 1994.

Prather, M.J., Lifetimes and eigenstates in atmospheric chemistry, Geophys. Res. Lett., 21, 801-804, 1994.

Prather, M., R. Derwent, D. Ehhalt, G.I. Pearman, P.J. Fraser, and R. Derwent, D. Ehhalt, P. Fraser, E Sanhueza, X. Zhou. Chapter 2: Other tracer gases and atmospheric chemistry, in Climate Change 1994, IPCC, J.T. Houghton et al., eds., Cambridge U. Press, pp. 73-126, 1995.

Steele, L.P., E.J. Dlugokencky, P.M. Lang, P.P. Tans, R.C. Martin, and K.A. Masarie, Slowing down of the global accumulation of atmospheric methane: depletion of OH radicals and the rise of emissions, Atmos. Environ. 19 397-407, 1985.