A perspective on time: loss frequencies, time scales and lifetimes

Michael J. Prather\textsuperscript{A,B} and Christopher D. Holmes\textsuperscript{A}

\textsuperscript{A}Earth System Science Department, University of California–Irvine, Irvine, CA 92697-3100, USA.
\textsuperscript{B}Corresponding author. Email: mprather@uci.edu

Environmental context. The need to describe the Earth’s system or any of its components with a quantity that has units of time is ubiquitous. These quantities are used as metrics of the system to describe the response to a perturbation, the cumulative effect of an action or just the budget in terms of sources and sinks. Given a complex, non-linear system, there are many different ways to derive such quantities, and careful definitions are needed to avoid mistaken approximations while providing useful parameters describing the system.

Abstract. Diagnostic quantities involving time include loss frequency, decay times or time scales and lifetimes. For the Earth’s system or any of its components, all of these are calculated differently and have unique diagnostic properties. Local loss frequency is often assumed to be a simple, linear relationship between a species and its loss rate, but this fails in many important cases of atmospheric chemistry where reactions couple across species. Lifetimes, traditionally defined as total burden over loss rate, are mistaken for a time scale that describes the complete temporal behaviour of the system. Three examples here highlight: local loss frequencies with non-linear chemistry (tropospheric ozone); simple atmospheric chemistry with multiple reservoirs (methyl bromide) and fixed chemistry but evolving lifetimes (methyl chloroform). These are readily generalised to other biogeochemistry and Earth system models.

Additional keywords: chemical modes, eigenvalues, global warming potentials.

Received 24 January 2013, accepted 9 April 2013, published online 30 May 2013

Introduction

The description of atmospheric chemistry and composition, or other components of the Earth’s system, using a scalar with units of time or inverse time is widespread.\cite{11-17} These quantities are often used as metrics of the system to describe the duration or decay of a perturbation, or even the cumulative effect of an action as in ozone depletion potential or global warming potential.\cite{8-12} There are many different ways to derive metrics of time, and they describe different properties of the system. Here we carefully define three of those metrics: loss frequency ($LF$) that is typically used in the continuity equation for loss of a species, time scale ($TS$) that can describe the e-fold of a perturbation to the system, and lifetime ($LT$) that is a budgetary term derived from integrated burden and loss. We demonstrate which properties of the system they describe. Three examples are taken from atmospheric chemistry and biogeochemistry, but they are readily generalised.

The confusion in deriving quantities with units of time to describe an Earth system is widespread.\cite{13,14,22,23} The use of metrics involving time is important cases of atmospheric chemistry where reactions couple across species. Lifetimes, traditionally defined as total burden over loss rate, are mistaken for a time scale that describes the complete temporal behaviour of the system. Three examples here highlight: local loss frequencies with non-linear chemistry (tropospheric ozone); simple atmospheric chemistry with multiple reservoirs (methyl bromide) and fixed chemistry but evolving lifetimes (methyl chloroform). These are readily generalised to other biogeochemistry and Earth system models.

Definitions and derivations

The continuity equation describing the rate of change of a species ($y$) at a given location ($x$) and time ($t$) can be written as:

$$\frac{dy(x,t)}{dt} = \text{production} (P)(x,t) - \text{loss} (L)(y,x,t) = p - LF \times y$$

(1)
The production rate is often assumed to be independent of $y$ and includes sources, in situ chemistry, transport and radiative terms, whereas the loss rate includes in situ chemistry, transport and other terms removing $y$ (see Prather[1]). The loss rate is often presumed to be a linear function of $y$, and hence the loss frequency ($LF$), with units of inverse time (i.e. year$^{-1}$), is calculated simply as $LF = L/y$. $LF$ is the eigenvalue of a one-box, linear system.

For many important cases, such as the example of tropospheric O$_3$ presented below, the linear form of Eqn 1 is substantially incorrect. For such non-linear systems the loss frequency may change as the system evolves, nevertheless a first-order accurate description of the system comes from the Taylor expansion of Eqn 1 about the current state ($y$).

$$\frac{d(\Delta y)}{dt} = \partial[P - L]/\partial y \times \Delta y + \text{order}(\Delta y^2)$$  \hspace{1cm} (2)

This corrected loss frequency, $LF = -\partial((P - L)(y))/\partial y$, is the partial derivative of the chemical terms and is evaluated at the current state ($y$) and for a one-box, non-linear system describes the decay (or growth) of a perturbation ($\Delta y$).

A time scale ($TS$) has units of time (e.g. year) and should describe the temporal behaviour of the system or perturbations to it, in the sense of an e-folding time for some component:

$$y(t) = a \times \exp[-t/TS] + \text{other terms}$$  \hspace{1cm} (3)

In this notation a negative time scale describes an unstable system. For a one-variable, one-box, constant-in-time, linear system, $TS = 1/LF$ and Eqn 3 is the solution to Eqn 1.

Most systems described by Eqn 1, however, exhibit multiple time scales that couple chemistry and transport across the system. These time scales are the inverse eigenvalues of a coupled linear system, also called mode times,[1,20,24–27] and the temporal behaviour of a single species usually involves multiple time scales, where $\sum \delta = 1$.

$$y(x,t) = y(x,0) \times \sum \delta \times \exp[-t/TS]$$  \hspace{1cm} (4)

A lifetime ($LT$) is an integrated quantity that characterises the overall budget or throughput of the system (e.g. emissions, losses) and has units of time (e.g. year). It is derived from the integral species ($Y \equiv \int y$, kg), production ($P \equiv \int p$, kg year$^{-1}$) and loss ($L \equiv \int loss = \int LF \cdot y$, kg year$^{-1}$) over the system. The instantaneous lifetime in atmospheric chemistry is defined as the integrated system-wide burden of a constituent divided by the integrated loss of that constituent ($LT \equiv Y/L$, year). In effect, the inverse lifetime is the weighted average of the loss frequencies ($<LF>$).

$$1/LT = L/Y = \left(\int LF \times y\right)/\left(\int y\right) = <LF>$$  \hspace{1cm} (5)

In general the lifetime is not a time scale of the system as defined in Eqs 3 and 4 but an amalgam of these time scales. An analogy would be the human lifetime: the time from birth to death contains a mix of times of growth, development and senescence, but one’s lifetime is an integral across these processes that cover very different types of activities. For the one-variable, one-box, constant-in-time, linear system, $LT = TS = 1/LF$.

Lifetimes can be defined for specific losses but always use the total burden. For example, if the total loss can be split among three processes, $L = L^a + L^b + L^c$, then the ‘a’ process lifetime, $LT^a \equiv YT^a$, and the inverse lifetimes are additive. In general, none of these are time scales of the system.

$$1/LT = L/Y = (L^a + L^b + L^c)/Y = 1/LT^a + 1/LT^b + 1/LT^c$$  \hspace{1cm} (6)

The steady-state lifetime ($LT^{SS}$) is a special case when production balances loss: i.e. $dy/dt = 0$ at the local scale, and $P = L = YLT^{SS}$ on the global scale. It is special also in that this lifetime represents the cumulative environmental effects of a pulse[28]: the time integral of effects (e.g. ozone depletion, surface air quality, radiative forcing) following an emission pulse of a species exactly equals the steady-state pattern of effects from that emission pattern multiplied by the steady-state lifetime of the perturbing species for that emission pattern, assuming the perturbation and decay can be linearised. These effects generally occur over a wide range of time scales (both faster and slower) than the steady-state lifetime. This leads to the somewhat confusing result that although the system-wide Eqn 7, which is used in assessments:

$$Y(t) \neq Y(0) \times \exp[-t/LT^{SS}]$$  \hspace{1cm} (7)

does not accurately describe the decay of a perturbation $Y(0)$, it still gives the exact integral of such a pulse and can be related to eigenvalue time scales (see Eqn 4).

$$\int_0^\infty Y(t) \, dt = Y(0) \times LT^{SS} = \sum \delta \times TS$$  \hspace{1cm} (8)

In non-linear systems, the lifetime of a perturbation ($\Delta$) to the burden ($Y$) can differ from the lifetime of the burden itself, i.e. $LT^Y \neq LT^Y \neq LT^\Delta$. The perturbation lifetime ($LT^\Delta$) describes the cumulative effect of a small pulse, and it differs from the base-state lifetime if the lifetime changes with burden. To derive $LT^\Delta$ consider the losses in a perturbed system, $L(Y + \Delta)$, to be the sum of the base-state loss defined as burden over lifetime plus that from the perturbation:

$$L(Y + \Delta) = Y/LT^Y + \Delta/LT^\Delta = (Y + \Delta)/LT^\Delta$$

$$= (Y + \Delta)/(LT^Y \cdot (1 + \Delta/Y) \cdot \partial \ln(LT)/\partial \ln(Y))$$  \hspace{1cm} (9)

$$LT^\Delta = LT^Y/(1 - \partial \ln(LT)/\partial \ln(Y)) + \text{order}(\Delta/Y) \equiv LT^Y \times f$$  \hspace{1cm} (10)

where the sensitivity of lifetime to burden is $s = \partial \ln(LT)/\partial \ln(Y)$, and the feedback factor on steady-state lifetime is $f = 1/(1 - s)$. For atmospheric CH$_4$, the feedback factor is $s = 1.4$; and for NO$_x$, it is $s = 0.92$. The perturbation lifetime is used correctly in climate and ozone assessments as a measure of the cumulative effect of a pulse emission, but it is often mistaken for the time scale (e-fold decay) of the pulse (i.e. Eqs 7–8). Thus, if the perturbation lifetime ($LT^Y \times f$) of CH$_4$ is 12 years, then a pulse of CH$_4$ decays with a mix of time scales both greater than and less than 12 years, but the integrated effect of such a pulse (Eqn 8) has a weighting factor of 12 years. See the example of CH$_4$Br and ozone depletion below. The loss frequency and time scales are inherent properties of the system, but the lifetime
A perspective on time

...and its variants depend on how the system is being forced with sources.

Another quantity with units of time, the age-of-air in the stratosphere,[31,32] or troposphere, [33] refers to the mean age (e.g. year) of an air mass since contact with some defined location (e.g. tropopause or surface). It is an integrative quantity like lifetime, only in this case the integral is over all transport paths that an air mass could have taken since the point of last contact to reach that location. Age-of-air is traditionally defined for conserved tracers; but a photochemical age-of-air could include chemical aging of the tracer in transit; and that is what we actually calculate when simulating for example the abundance of chlorofluorocarbons (CFCs) in the stratosphere. Age-of-air, like lifetime, does not describe local frequencies nor the time scales of the system. For example, the age-of-air in the upper stratosphere and mesosphere is typically 40% or more larger that the e-fold time scale for removal of a conserved tracer from the stratosphere.[6]

Case studies

Loss frequencies, linearisation and tropospheric O₃

Tropospheric ozone (O₃) provides a great example of the problems in deriving loss frequencies. The photochemistry of O₃ is coupled through families of radicals (e.g. HO₂, NO₂), and the simplistic linear assumptions often used to calculate the loss frequency or time scales of O₃ are often significantly in error. Several studies have derived eigenvalues and modes for the ozone mechanism.[1] In the troposphere, the second largest loss is NO (O₃ + NO → NO₂ + O₂), followed by rate 2 (O₃ + NO₂ → HO₂ + O₂) and thermally decomposes to NO₂ in the boundary layer, count...
The absolute north–south gradient frequency to evaluate \(O_3\) as a tagged tracer, such as following the stratospheric influx of \(O_3\) to the surface or estimating the long-range transport of pollution. In both cases the decay of the tagged \(O_3\) is underestimated. In the opposite sense, the use of tagged tracers for CO can overestimate the decay rate because the added CO reduces OH abundances and thus its own loss frequency. Table 1 is only an example; accurate simulation of \(O_3\) perturbations with a chemistry transport model would require linearisation of the chemical system (tangent linear model) at each time step at each location.

**From lifetimes to time scales with CH\(_3\)CCl\(_3\)**

The trace gas CH\(_3\)CCl\(_3\) (methyl chloroform, 1,1,1-trichloroethane) provides a case study in which the lifetime of the gas shifts as its atmospheric distribution evolves in response to changing emissions and atmospheric accumulation. Methyl chloroform is an industrially produced ozone-depleting halocarbon. Its abundance peaked in the early 1990s with a 30–60 ppt due to the pre-

Methyl bromide (CH\(_3\)Br) presents an interesting case study of loss frequencies, time scales and lifetimes because the chemistry can be treated as fully linear but the interplay of different reservoirs (stratosphere, troposphere, ocean mixed layer) creates non-intuitive results. Methyl bromide is a naturally occurring gas with oceanic sources. Its production and use in agriculture and fumigation has increased its atmospheric abundance, and the bromine radicals it releases in the stratosphere (Br\(_{\text{v}}\)) can cause ozone depletion. Formal treatment of the CH\(_3\)Br system identified lifetimes and time scales that were not directly recognisable from the local loss frequencies. Here, we revisit that work but collapse the 1-D chemistry diffusion problem into a three-box model with chemical model and exchange coefficients as summarised in Table 2. On the far right column of Table 2 is shown the mole fraction of CH\(_3\)Br in the three reservoirs at steady-state with troposphere-only sources (scaled to 1 ppt in the troposphere). The ocean layer is equivalent to 2.9\% of the atmosphere, based on a 100-m mixed layer and the solubility of CH\(_3\)Br.

The eigenvalue decomposition of the system with six degrees of freedom is given in Table 3. Because Br\(_{\text{v}}\) does not feedback on CH\(_3\)Br in this simplified system, there are only three CH\(_3\)Br eigenvalues. These three time scales of 3.2, 0.92 and 0.018 years differ substantially from the inverse loss frequencies for CH\(_3\)Br because the exchange rates between reservoirs play a key role in determining the time scales of the system. The coefficients for
A perspective on time

Table 2. Parameters defining 3-box chemical model for CH₃Br–BrY system

Notes: loss frequencies and exchange rates for the 3-box model chosen to match the 1-D diffusion model of Prather[46]; 1 atm = 1.765 x 10²⁰ moles of dry air; 14.1 Tg Br ppt-atm⁻¹. The cases shown for troposphere-only and ocean-only emissions are scaled to 10-ppt tropospheric CH₃Br, as is the last case (C) for which the mix of troposphere and ocean emissions yields a 100% supersaturation (neutral) ocean layer. For evolution of atmospheric and oceanic CH₃Br see Yvon-Lewis and Butler,[45] Butler[47] and Hu et al.[48]

<table>
<thead>
<tr>
<th>Boxes</th>
<th>Mass (atm)</th>
<th>Exchange (atm year⁻¹)</th>
<th>CH₃Br loss frequency (year⁻¹)</th>
<th>BrY loss frequency (year⁻¹)</th>
<th>CH₃Br steady-state troposphere (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stratosphere</td>
<td>0.128</td>
<td></td>
<td></td>
<td></td>
<td>0.569</td>
</tr>
<tr>
<td>Stratosphere–Troposphere</td>
<td></td>
<td>0.023</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Troposphere</td>
<td>0.872</td>
<td>0.607</td>
<td>52</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Troposphere–Ocean</td>
<td></td>
<td>0.730</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ocean layer</td>
<td>0.029</td>
<td>29.2</td>
<td>104</td>
<td>0.463</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Eigenvalue decomposition of 3-box, 2-species system, showing coefficients (ppt) of eigenvalue time scales for 1-ppt tropospheric CH₃Br pulse

<table>
<thead>
<tr>
<th>Eigenvectors with CH₃Br and BrY</th>
<th>Eigenvectors with only BrY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eigenvalue (year⁻¹)</td>
<td>Time scale (years)</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>0.3095</td>
</tr>
<tr>
<td>Stratosphere</td>
<td>0.2311</td>
</tr>
<tr>
<td>Troposphere</td>
<td>0.0079</td>
</tr>
<tr>
<td>Ocean</td>
<td>0.0037</td>
</tr>
<tr>
<td>BrY</td>
<td>-0.2421</td>
</tr>
<tr>
<td>Stratosphere</td>
<td>0.0000</td>
</tr>
<tr>
<td>Troposphere</td>
<td></td>
</tr>
<tr>
<td>Ocean</td>
<td></td>
</tr>
</tbody>
</table>

Note that each time scale following a single pulse of 1 ppt CH₃Br in the troposphere are given in Table 3. The abundances of CH₃Br in the troposphere (trp) and stratosphere (str) follow three exponential decay curves

\[
\text{trp-CH₃Br}(t) = 0.985 \, e^{-t/0.92} + 0.008 \, e^{-t/3.2} + 0.007 \, e^{-t/0.018} \quad (11)
\]

\[
\text{str-CH₃Br}(t) = -0.231 \, e^{-t/0.02} + 0.231 \, e^{-t/3.2} + 0.000 \, e^{-t/0.018} \quad (12)
\]

Note that trp-CH₃Br decays rapidly with 0.92 years e-fold, but then ~1% decays with the much longer 3.2 years e-fold that is tied to the decay of str-CH₃Br. The str-CH₃Br abundance builds initially as the CH₃Br reaches the stratosphere and then decays with the single longest-lived chemical mode time for CH₃Br of 3.2 years. Stratospheric BrY, effectively a proxy for ozone depletion, has more complex behaviour due to the time scale for stratosphere–troposphere exchange.

\[
\text{str-BrY}(t) = +0.210 \, e^{-t/5.6} - 0.242 \, e^{-t/3.2} + 0.032 \, e^{-t/0.92} + 3 \, \text{more small terms} \quad (13)
\]

Note the str-BrY takes longer than str-CH₃Br to reach its peak, and then it takes much longer to decay with a time scale of 5.6 years. These are the true time scales of the system, and not readily predicted from the loss frequencies alone.

The steady-state lifetimes derived from the budgets are given in Table 4 for three different cases with tropospheric CH₃Br abundances of 10 ppt: (a) a hypothetical, troposphere-only source giving an ocean saturation level of 46% (i.e., 4.6 ppt); (b) a hypothetical, ocean-only source giving an ocean saturation level of 177% and (c) a mix of both sources to yield a net neutral ocean saturation of 100%. During the peak of anthropogenic emissions in the 1990s, ocean saturation was about 85%[45–47] and following mitigation the abundance dropped to ~8 ppt with average ocean saturation of 100%.[48] Note that this drop of 20% in CH₃Br tropospheric abundance requires reduction of more than 50% in tropospheric emissions. The steady-state lifetime, 1.03 years in case A and 0.50 in case B, is straightforward. In case C the combination gives an intermediate lifetime of 0.70 years. Thus we have a clear and obvious case where the lifetime depends on the source.

The steady-state lifetime and pattern for a tropospheric source are important numbers in that they describe exactly the integral of exposure (e.g. ppt-year) following a single
although the lifetime of the CH$_3$Br source is only
note that the ozone depletion persists for more than 5 years
degrees of freedom (e.g. CH$_3$Br); however, proper diagnosis even in
relatively simple systems, time scales reflect the multitude of
effects.

Loss frequency is often used as a simple scaling factor, relating the
local loss rate of a species to its abundance. In general with coupled,
multi-species systems, the simple linear scaling fails, but an effec-
tive loss frequency can be calculated for a perturbation to a species
following the release but it fails to describe the time scales of
those effects.

Conclusions
Loss frequency is often used as a simple scaling factor, relating the
local loss rate of a species to its abundance. In general with coupled,
multi-species systems, the simple linear scaling fails, but an effect-
ive loss frequency can be calculated for a perturbation to a species
with a linearisation of the system (e.g. tropospheric O$_3$). Lifetimes,
which are defined in terms of integrated budgets, depend on the
method of external forcing. The lifetime of a trace gas can change
even when the chemical reactivity of the atmosphere is unchanged
(e.g. CH$_3$CCl$_3$). For a perturbation forced by a specific emission
pattern, the product of the steady-state pattern and the lifetime are an
exact integral of a pulse of that emission, including any consequent
environmental effects (e.g. CH$_3$Br and O$_3$ depletion). This
method of defining lifetime works even for trace gases with known
chemical feedbacks or indirect effects such as N$_2$O, CH$_4$ and
NO$_x$ as long as one uses the perturbation lifetime. Even for relatively
simple systems, time scales reflect the multitude of
degrees of freedom (e.g. CH$_3$Br); however, proper diagnosis even in
3-D models can identify the correct response to perturba-
tions.
The often-made simplifying assumption – that these
three metrics are the same – may be appealing if one is sure that
the errors are small, but the lack of rigor may propagate to systems
where much larger, unrecognised errors will occur.

Acknowledgements
This research was supported by the NASA Modelling, Analysis, and
Prediction Program (NNX09AJ47G), the Office of Science (BER) of the US
Department of Energy (DE-SC0007021), and the Kavli Chair in Earth
System Science.

Table 4. Steady-state budgets and lifetimes under different emissions scenarios

<table>
<thead>
<tr>
<th>Case</th>
<th>A: troposphere source</th>
<th>B: ocean source</th>
<th>C: current (100% supersaturation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>CH$_3$Br</td>
<td>Br$_Y$</td>
<td>CH$_3$Br</td>
</tr>
<tr>
<td>Source</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Troposphere (Tg year$^{-1}$)</td>
<td>131</td>
<td>0</td>
<td>76</td>
</tr>
<tr>
<td>Ocean (Tg year$^{-1}$)</td>
<td>0</td>
<td>289</td>
<td>120</td>
</tr>
<tr>
<td>Stratosphere (ppt)</td>
<td>5.7</td>
<td>4.4</td>
<td>5.7</td>
</tr>
<tr>
<td>Troposphere (ppt)</td>
<td>10.0</td>
<td>0.1</td>
<td>4.4</td>
</tr>
<tr>
<td>Ocean (ppt)</td>
<td>4.6</td>
<td>1.1</td>
<td>7.7</td>
</tr>
<tr>
<td>Burden (Tg year$^{-1}$)</td>
<td>134.8</td>
<td>142.9</td>
<td>137.6</td>
</tr>
<tr>
<td>Loss</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stratosphere (Tg year$^{-1}$)</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Troposphere (Tg year$^{-1}$)</td>
<td>74.5</td>
<td>74.5</td>
<td>74.5</td>
</tr>
<tr>
<td>Ocean (Tg year$^{-1}$)</td>
<td>55.1</td>
<td>213.0</td>
<td>119.6</td>
</tr>
<tr>
<td>Steady-state lifetime (years)</td>
<td>1.029</td>
<td>0.495</td>
<td>0.703</td>
</tr>
</tbody>
</table>

References
[2] B. Bolin, H. Rodhe, Note on concepts of age distribution and transit-
time in natural reservoirs. Tellus 1973, 25, 58. doi:10.1111/j.2153-
1994.T01-4-00064.X
halocarbon radiative forcing and global warming potentials. J. Geo-
phys. Res. – Atmos. 1995, 100, 1271. doi:10.1029/94JD02516
doi:10.1038/357033A0
[11] D. J. Wuebbles, Weighing functions for ozone depletion and
1994, Intergovernmental Panel on Climate Change (Eds J. T. Houghton,
L. G. Meira-Filho, J. Bruce, H. Lee, B. A. Callander, E. Hates, N. Harris,
Fahey, J. Haywood, J. Lean, D. C. Lowe, G. Myhre, J. Nganga,
R. Prinn, G. Raga, M. Schulz, R. Van Dorland, Changes in atmo-
spheric constituents and in radiative forcing in Climate Change 2007:
The Physical Science Basis Fourth Assessment Report of the Inter-
governmental Panel on Climate Change (Eds S. Solomon, D. Qin,
M. Manning) 2007, pp. 129–234 (Cambridge University Press:
Cambridge UK).
Meteorological Organization: Geneva, Switzerland).