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Lifetimes of atmospheric species: Integrating environmental impacts

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[1] The environmental damage caused by atmospheric pollutants is proportional to the duration of their effects. The global impacts of greenhouse gases (as measured by global warming potential) and ozone depleting substances (as measured by ozone depletion potential) have traditionally been calculated using the atmospheric lifetime of the source gas as a quantitative measure of the impact's duration, assuming that the gas quickly reaches a steady-state pattern which decays exponentially according to the lifetime. This assumed behavior obviously does not match the true rise and fall of impacts, particularly secondary ones like ozone depletion, that can be seen in numerical integrations or chemical mode decomposition. Here, the modes decomposition is used to prove that: (a) the steady-state pattern of impacts caused by specified emissions, multiplied by (b) the steady-state lifetime of the source gas for that emission pattern, is exactly equal to (c) the integral of all impacts - independent of the number and atmospheric residence times of secondary impacts.   INDEX TERMS: 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325); 6620 Public Issues: Science policy; 6309 Policy Sciences: Decision making under uncertainty. **Citation:** Prather, M. J., Lifetimes of atmospheric species: Integrating environmental impacts, *Geophys. Res. Lett.*, *29*(22), 2063, doi:10.1029/2002GL016299, 2002.

1. Lifetimes

[2] Efforts to codify time scales in the Earth system have recognized a range of useful diagnostics involving units of time [*Bolin and Rodhe*, 1973; *O'Neill et al.*, 1994]. The most often used time scale for atmospheric gases is the average global lifetime (L, with units, e.g., yr), which is defined by terms in the global budget as the ratio of the total atmospheric burden (B, kg) to total sink (S, kg/yr), $L = B/S$, rather than by the temporal behaviour of the system. For gases with globally uniform loss frequencies, such as radioactive decay of radon, the lifetime is equal to the inverse of the loss frequency. For gases with a range of local loss frequencies, such as photodissociation of chlorofluorocarbons in the stratosphere, the lifetime averages over the loss frequencies of different chemical domains. At steady-state, the sink rate equals the emission rate (E, kg/yr) by definition, and the steady-state lifetime (L^{SS}) can be calculated from either sink or emissions:

$$L^{SS} = B/S = B/E \qquad (1)$$

[3] The true temporal behaviour of the system, as seen by the decay of perturbations, involves a range of e-fold times, none of which is equal to the steady-state lifetime. Decomposing perturbations into the eigenvectors of the linearized chemistry-transport system shows that atmospheric chemistry responds to additional emissions with a wide range of e-fold times equal to the inverse of the negative eigenvalues [*Prather*, 1996, 1997]. The predicted existence of these chemical modes with their characteristic e-fold times were subsequently demonstrated in three-dimensional global tropospheric chemistry models [*Wild and Prather*, 2000; *Derwent et al.*, 2001]. In these studies the steady-state lifetime was identified as the key scaling factor to integrate over all time scales.

[4] The accepted measure of the total impact of emissions of both greenhouse gases (as measured by the global warming potential, GWP) and ozone depleting substances (as measured by the ozone depletion potential, ODP) is calculated by integrating over impacts (either radiative forcing or ozone depletion) following a pulsed emission. 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 ozone depletion. International assessments have traditionally calculated these potentials using the atmospheric lifetime of the source gas as a quantitative measure of the impact's duration, assuming that the gas quickly reaches a steady-state pattern that decays exponentially according to the lifetime [*Houghton et al.*, 1995; *WMO*, 1995; *Solomon et al.*, 1992]. This assumed behavior obviously does not match the true rise and fall of impacts, particularly secondary ones. For example, there is considerable misunderstanding about the use of the steady-state lifetime of the primary source gas as the scaling factor, specifically that it does not apply to extremely short-lived gases (e.g., 1-C_3H_7Br with a tropospheric residence time of weeks [*Bridgeman et al.*, 2000; *Olsen et al.*, 2000, *Wuebbles et al.*, 2001]) whose intermediate products may survive much longer in the atmosphere (e.g., Br with a stratospheric residence time of years [*Ko et al.*, 1997]). The applicability of the steady-state lifetime is readily shown using the formalism of chemical modes.

2. Decomposition into Modes

[5] A pulse (P, kg) of species X produces a unique decomposition (by coefficients A_i^P, units of mole fraction, ppb) into chemical modes (eigenvectors V_i, dimensionless, describing the relative spatial pattern of all species). Each mode has its own characteristic e-fold time (T_i, units of time, yr). The resulting space-time pattern following the pulse is given by a sum over all decaying modes i, where $X_P(z, t)$ is the abundance (ppb) of species X at location z

(multi-dimensional) and time t, and where the chemical modes $V_i(z, X)$ are a subset of the eigenvectors of the complete system that explicitly include species X.

$$X_P(z,t) = \sum_{modes\ i} \left[A_i^P V_i(z,X) \exp(-t/T_i) \right] \qquad (2)$$

For a general Earth system, not necessarily in steady state, these equations describe exactly the behaviour of a perturbation whose amplitude is within the linearization of the system. All the eigenvalues are negative or zero unless the system is unstable to infinitesimal perturbations.

[6] To relate the spatial pattern to the budget quantities, the distribution is integrated over space (dz) with a weighting factor ($wt(z)$, units of kg/ppb per unit space) to calculate the initial burden of X ($B(X_P,0)$, kg), which equals the initial pulse.

$$B(X_p, t=0) = \int X(z, t=0) wt(z) dz = \sum_{modes\ i} \left[A_i^P W_i(X) \right] = P \qquad (3)$$

The relative content of X in each chemical mode is expressed by W_i (kg/ppb).

$$W_i(X) = \int V_i(x, Z) wt(z) dz \qquad (4)$$

3. The Steady State

[7] Now consider continuous emission (E, kg/yr) in the same pattern as the pulse P at a rate P/Δ, where Δ (yr) is an arbitrary time interval. This continuous emission excites the chemical modes in the same relative amplitudes as did the pulse, and it can be integrated from $t = -\infty$ to 0 to get the steady-state distribution. Note that the steady-state accumulation X results in each mode being weighted by its e-fold time.

$$X_{E=P/\Delta}^{SS}(z) = \int_{-\infty}^{0} X_P(z,t) dt / \Delta$$
$$= \sum_{modes\ i} \left[A_i^P V_i(z,X) \left\{ \int_{-\infty}^{0} \exp(t/T_i) dt \right\} / \Delta \right]$$
$$= \sum_{modes\ i} \left[A_i^P V_i(z,X) T_i / \Delta \right] \qquad (5)$$

The instantaneous loss frequency for each mode is just $1/T_i$, and thus the steady-state burden, sink, and lifetime can be easily calculated from the modes. The steady-state lifetime depends on the pattern of emissions (i.e., on the A_i^P) but not the absolute magnitude.

$$B_{E=P/\Delta}^{SS}(X) = \sum_{modes\ i} \left[A_i^P W_i(X) T_i / \Delta \right] \qquad (6)$$

$$S_{E=P/\Delta}^{SS}(X) = \sum_{modes\ i} \left[\{ A_i^P W_i(X) T_i / \Delta \} / T_i \right]$$
$$= \sum_{modes\ i} \left[A_i^P W_i(X) / \Delta \right] \qquad (7)$$

$$L_{E=P/\Delta}^{SS}(X) = \sum_{modes\ i} \left[A_i^P W_i(X) T_i / \Delta \right] / \sum_{modes\ i} \left[A_i^P W_i(X) / \Delta \right]$$
$$= \sum_{modes\ i} \left[A_i^P W_i(X) T_i \right] / \sum_{modes\ i} \left[A_i^P W_i(X) \right] \qquad (8)$$

4. Integrating Over a Pulse

[8] Using the relationship between steady-state lifetime, burden, and emission rate,

$$L_{E=P/\Delta}^{SS}(X) / B_{E=P/\Delta}^{SS}(X) = 1/E = \Delta/P \qquad (9)$$

one can show that the integrated impact of a single pulse $\int X_P dt$ (in ppb-yr) with (a) the same release pattern as the steady-state emissions and (b) the same burden as the steady-state distribution is readily calculated from the modes. The integrated abundances per unit pulse have the exact pattern of the steady-state distribution (ppb) multiplied by the steady-state lifetime (yr).

$$\int_0^{\infty} X_P(z,t) dt / P = \sum_{modes\ i} \left[A_i^P V_i(z,X) \int_0^{\infty} \exp(-t/T_i) dt \right] / P$$
$$= \sum_{modes\ i} \left[A_i^P V_i(z,X) T_i \right] / P = X_{E=P/\Delta}^{SS}(z) \Delta / P$$
$$= X_{E=P/\Delta}^{SS}(z)\ L_{E=P/\Delta}^{SS}(X) / B_{E=P/\Delta}^{SS}(X) \qquad (10)$$

[9] Suppose that the photochemical breakdown of species X begets a secondary species Y that has an impact. Can the integrated impact caused by Y be calculated with the same method using the lifetime of X? The pattern and decay of the Y perturbation, like that of X, can be expressed as a sum of modes. The sum may be over a different, but overlapping range of modes j. The key point here is that the coefficients of the modes (A_j^P) are determined uniquely by the pulse of X since we begin with $Y = 0$ everywhere. (If we were driving the perturbation by emissions of Y this scaling would be different.)

$$Y_P(z,t) = \sum_{modes\ j} \left[A_j^P V_j(z,Y) \exp(-t/T_j) \right] \qquad (11)$$

The steady-state buildup of Y is calculated like that of X.

$$Y_{E=P/\Delta}^{SS}(z) = \int_{-\infty}^{0} Y_P(z,t) dt / \Delta = \sum_{modes\ j} \left[A_j^P V_j(z,Y) T_j / \Delta \right] \qquad (12)$$

The integrated impact of species Y for this single pulse, $\int Y_P dt$ (in ppb-yr), has the steady-state pattern for Y but scales with the steady-state lifetime of X, the species driving the perturbation.

$$\int_0^{\infty} Y_P(z,t) dt / P = \sum_{modes\ j} \left[A_j^P V_j(z,Y) T_j \right] / P$$
$$= Y_{E=P/\Delta}^{SS}(z) \Delta / P$$
$$= Y_{E=P/\Delta}^{SS}(z)\ L_{E=P/\Delta}^{SS}(X) / B_{E=P/\Delta}^{SS}(X) \qquad (13)$$

[10] An example of this scaling can be found in the model of the (CH$_3$Br, Br$_Y$)-system derived in *Prather* [1997], which includes a simple stratosphere, troposphere, and oceanic mixed layer. The steady-state lifetime of CH$_3$Br for surface emissions is 1.03 yr, but the longest mode's decay time of CH$_3$Br from the atmosphere is 1.83 yr, with the final reservoir being the lower stratosphere. The longest

mode of Br_Y depends on stratospheric turnover and was even longer, 4.5 yr in this model. A steady-state pattern of CH_3Br surface emissions that led to a surface abundance of 1 ppt gave a Br_Y abundance of 0.42 ppt at 20 km altitude - presumed to be the measure of ozone depletion. When the entire burden of CH_3Br contained in the 1-ppt steady-state atmosphere is released at the surface, the 20-km Br_Y abundance begins at 0 ppt, rises slowly after 6 years to a maximum of about 0.07 ppt (at which time there is almost no CH_3Br left in the troposphere), and decays eventually with an e-fold of 4.5 yr (see Figure 8 of *Prather* [1997]). Over half of the integrated ozone depletion occurs more than 7 years after the emission. The integral under this curve is 0.43 ppt-yr, exactly the product of 0.42 ppt and 1.03 yr. The fact that the steady-state pattern of the secondary product and lifetime of the primary gas give the exact integral was proposed in that paper and is now proven in this one.

5. Conclusions

[11] The steady-state lifetime of the source gas is the scaling factor for all impacts driven by the source gas, including secondary impacts. Likewise the steady-state pattern used to assess damage is that created by the emission pattern of the source gas. Unlike the modes, the steady-state lifetime is not a general property of the atmosphere and can be very sensitive to the emission pattern [*Prather*, 1998; *Bridgeman et al.*, 2000; *Olsen et al.*, 2000, *Wuebbles et al.*, 2001]. Effectively, the possibility of much longer lifetimes for the secondary products than the primary source gas is taken into account by the steady-state distribution of the secondary products.

[12] This derivation not only solidifies past approximations for GWPs and ODPs of long-lived source gases but also establishes the foundation for calculating the environmental impacts of short-lived gases. The cumulative impacts can be evaluated taking the steady-state impact and scaling by the steady-state lifetime of the source gas. This method is far more practical than trying to integrate the impacts over the full duration of the perturbation (at least several years). Both simulations - the steady-state forced by constant emissions and the transient driven by a pulse - contain the same information and require that the model integrate over the duration of all impacts, including the time scales for secondary products. The basic uncertainty in evaluating these impacts still remains our ability to model difficult processes, like convection and scavenging, that control the distribution of short-lived species [*Ko et al.*, 1997; *Bridgeman et al.*, 2000; *Olsen et al.*, 2000, *Wuebbles et al.*, 2001].

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