

Time Scales in Atmospheric Chemistry: Coupled Perturbations to N₂O, NO_y, and O₃

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Nitrous oxide (N₂O) is one of the top three greenhouse gases whose emissions may be brought under control through the Framework Convention on Climate Change. Current understanding of its global budget, including the balance of natural and anthropogenic sources, is largely based on the atmospheric losses calculated with chemical models. A representative one-dimensional model used here describes the photochemical coupling between N₂O and stratospheric ozone (O₃), which can easily be decomposed into its natural modes. The primary, longest lived mode describes most of the atmospheric perturbation due to anthropogenic N₂O sources, and this pattern may be observable. The photolytic link between O₃ and N₂O is identified as the mechanism causing this mode to decay 10 to 15 percent more rapidly than the N₂O mean atmospheric lifetime, affecting the inference of anthropogenic sources.

Natural modes in atmospheric chemistry are general solutions of the continuity equations that describe how chemical species build up and decay. Each mode is a pattern in the global distribution of all chemical species (1–3). They can be used to diagnose atmospheric perturbations and their environmental impact through their decay times (4). For example, emissions of N₂O excite many atmospheric chemical modes, most of which decay in a few years, leaving behind unique long-term, century-scale perturbations to N₂O, NO_y (5), and O₃ that decay in unison. This group is fully coupled through stratospheric photochemistry: N₂O emitted at the surface enters the stratosphere and releases NO_y, which catalytically destroys O₃ in the mid-stratosphere; as a result, more ultraviolet sunlight is available for photolytic destruction of N₂O. By explicitly representing the dependence of the photolysis rates on overhead O₃ abundance and by directly calculating all atmospheric modes with a one-dimensional (1D) model, we show here how photolytic coupling leads to a more rapid decay of N₂O perturbations than anticipated from the N₂O lifetime based on steady-state budgets.

Nitrous oxide, the third most important greenhouse gas in terms of anthropogenic climate forcing, is also one of the more important trace gases in driving atmospheric chemistry (6). Unfortunately, its global budget, and in particular the cause of its steady rise over the past century, is not well defined. N₂O has increased from 275 ppbv in the preindustrial era to 311 ppbv today (7). The anthropogenic sources for this increase are probably not all identified and certainly not well quantified. The current rate of excess accumulation of N₂O in the atmosphere defines part of this source [3.9

Tg of N per year (TgN/year)], and the other part is derived from the increase since the industrial era divided by the lifetime (1.4 TgN/year). The N₂O budget is based on the steady-state lifetime derived from chemical models as constrained by the observed distribution (8). It does not recognize that recent increases to atmospheric N₂O (teragrams of N) might be governed by loss frequencies (per year) that differ from the inverse of the steady-state mean lifetime.

In the case of methane (CH₄), the second most important greenhouse gas, we have seen how local chemical coupling with CO and OH generates modes with time scales similar to, but longer than, the instantaneous chemical lifetimes of CH₄ and CO (1). Thus, with a steady-state lifetime of 8.6 years, a CH₄ perturbation actually decays by a factor of e (e-folds) in 12.2 years, greatly enhancing the climate impact of incremental CH₄ emissions. In the case of CH₃Br, an important ozone-depleting substance, we have seen how the transport between different chemical environments produces long-lived modes that, once again, decay more slowly than expected from the steady-state lifetime (4). In this case, a 1D

diffusion model with fixed, linear chemistry for CH₃Br was used to couple the different chemical regimes of the stratosphere, the troposphere, and an ocean layer. For surface emissions, the CH₃Br lifetime is about 1.0 year, yet the primary mode decays with an e-fold time of 1.8 years. In contrast to these chemical systems for which the primary mode decays more slowly than predicted by the steady-state lifetime, Fisher (9) argued that perturbations to N₂O would decay more rapidly than the steady-state lifetime for the reasons given above.

Here we applied eigenvalue analysis (2) to the {N₂O, NO_y, O₃} system to derive the long-lived natural mode that couples perturbations to all three species. A 1D vertical-diffusion model of the stratosphere and troposphere—similar to those used in ozone depletion studies two decades ago (4, 10)—was used so that all modes could be explicitly calculated. The best current 2D and 3D chemistry-transport models include all of the photochemical mechanisms discussed here, but they have so many degrees of freedom that the linear decomposition needed for the eigenvalue analysis is not possible. Furthermore, the number of modes, equal to the number of degrees of freedom, is so great as to preclude a complete solution.

Chemical modes are based on a linearization of the tendency equation for each chemical species at each location in time (2, 3). Let the vector **X**^{*j*} describe the mixing ratio of the three species N₂O, NO_y, and O₃ at atmospheric level *j*, then the vector continuity equation at each level can be expressed simply.

$$d\mathbf{X}^j/dt = \mathbf{C}^j + d/dz(K^j N^j d\mathbf{X}^j/dz) \quad (1)$$

The local net chemical change of the three species at level *j* is denoted vector **C**^{*j*}, and the second term is the divergence of the vertical diffusive flux (*K*^{*j*} is the diffusion coefficient, and *N*^{*j*} the atmospheric density). The Jacobian of this system is defined by **J**_{*jk*} ≡ ∂(d**X**^{*j*}/dt)/∂**X**^{*k*}, and each *jk*'th 3×3

Fig. 1. Schematic of the {N₂O, NO_y, O₃} system Jacobian. **X**^{*j*} is a vector of the three species {N₂O, NO_y, O₃} at atmospheric level *j* = 1 (surface) to *n* (top of atmosphere). Each element (bold) is a 3×3 matrix representing a component of the partial derivative of the three continuity equations for each species at that level

∂(d X ¹ /dt):	B	B	R	R	...	R	R	R	R	
∂(d X ² /dt):	T	P+T+R	T+R	R	...	R	R	R	R	
∂(d X ³ /dt):	0	T	P+T+R	T+R	...	R	R	R	R	
...										
∂(d X ^{<i>n-2</i>} /dt):	0	0	0	0	...	T	P+T+R	T+R	R	
∂(d X ^{<i>n-1</i>} /dt):	0	0	0	0	...	0	T	P+T+R	T+R	
∂(d X ^{<i>n</i>} /dt):	0	0	0	0	...	0	0	B	B	
						∂ X ¹	∂ X ²	∂ X ³	∂ X ⁴	
							∂ X ^{<i>n-3</i>}	∂ X ^{<i>n-2</i>}	∂ X ^{<i>n-1</i>}	∂ X ^{<i>n</i>}

(rows) with respect to each species at other levels (columns): **0** = null matrix; **P** = local chemistry; **T** = transport (1D diffusion); **R** = radiative coupling; and **B** = boundary conditions (includes all types of coupling). The **R** matrix includes only terms from O₃ overhead.

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block is outlined schematically in Fig. 1. The eigenvectors and eigenvalues of \mathbf{J} are the natural modes and inverse time scales of the system, respectively. Local chemistry and transport result in a block-tridiagonal system [only \mathbf{P} , \mathbf{T} , and \mathbf{B} blocks as for the CH_3Br system as in (4)]; whereas the photolytic feedbacks—the dependence of \mathbf{C}^j on the overhead O_3 column—fill in the upper triangular part (\mathbf{R} blocks) as shown in Fig. 1. A typical observed mid-latitude profile for N_2O , NO_y , and O_3 is used as the reference case (11). The chemical terms are calculated and linearized about this reference atmosphere and the diffusion terms adjusted to give reasonable profiles for N_2O , NO_y , and O_3 (12) (Fig. 2). The resulting steady-state lifetime for N_2O forced by surface emissions is 127 years, which is close to currently accepted values (8).

We consider an N_2O -alone system (14×14 Jacobian) by fixing NO_y and O_3 and calculating the 14 modes that encompass a linearly independent set of vertical profiles of N_2O . The time scales of the longer lived modes are then 125 years (primary), 2.0 years (secondary), and 0.57 year (tertiary). The steady-state profile from surface emissions, when decomposed into these 14 modes, is almost entirely represented by the primary mode. For N_2O , unlike for CH_4 and CH_3Br as described above, there is little difference between the steady-state lifetime and the time scale of the primary mode: first, N_2O has no significant tropospheric loss, and second, the time scale for removal of N_2O is much longer than those for atmospheric mixing.

The complete Jacobian (14 atmospheric levels and three species) is a 42×42 matrix with 42 modes. The primary mode with an e-fold time of about 100 years couples all three species, and the next longest lived mode has an e-fold time of about 3 years. The role of photolytic feedbacks is studied readily with this 1D system by noting how the primary mode is altered by specific coupling terms in the Jacobian. Consider a sequence of four hypothetical chemistries for

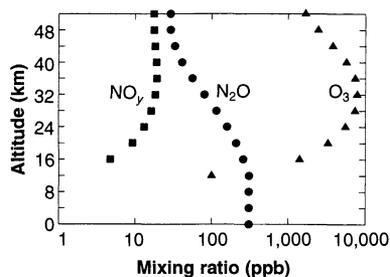


Fig. 2. Steady-state profiles (in parts per billion) of N_2O (circles), NO_y (squares), and O_3 (triangles) as a function of altitude calculated from a 1D model (12).

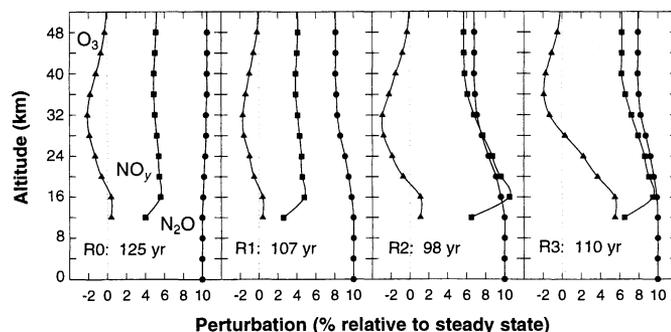
the $\{\text{N}_2\text{O}, \text{NO}_y, \text{O}_3\}$ -system as illustrated in Fig. 3 where the primary mode is scaled to represent a 10% perturbation to N_2O at the surface (31 ppbv). Case R0 includes only local chemistry (that is, no \mathbf{R} blocks in Fig. 1), and 14 of its 42 modes are identical in N_2O -space to the 14 N_2O -alone modes above but also contain related NO_y and O_3 perturbations. The time scale, 125 years, is the same as for N_2O alone, the relative perturbation to N_2O is almost uniform with altitude, and the NO_y perturbation is half that of N_2O . Case R1 includes those terms coupling depletion in overhead O_3 with increased loss of N_2O through photolysis and reaction with $\text{O}(^1\text{D})$. The time scale drops dramatically to 107 years, and the relative perturbation to N_2O falls off with altitude. Case R2 includes an additional radiative coupling: that between changes in overhead O_3 and NO_y chemistry. The time scale drops further to 98 years, the NO_y relative perturbation doubles and is now comparable to the N_2O perturbation, and the O_3 perturbation has increased in response to NO_y . Case R3 uses all possible radiative couplings, including the ozone self-healing effect (10) whereby O_3 depletion in the upper stratosphere allows greater penetration of ultraviolet radiation that photolyzes molecular oxygen, making more O_3 in the mid and lower stratosphere. This coupling reverses the O_3 perturbation below 36 km. The time scale rises to 110 years, but the perturbations to N_2O and NO_y are not greatly changed. This final pattern (R3) specifies the vertical profile of changes to N_2O , NO_y , and O_3 expected from the ~ 35 ppbv increase in N_2O over the past 100 years.

How would a single surface emission of 1000 kg of N_2O be represented by the 42 natural modes? The inverse of the matrix consisting of all the mode vectors multiplied by the initial perturbation yields the coefficients for each mode. The principal long-lived modes contain most of the net

content of the N_2O pulse; the short-lived, rapid-transport modes have large but canceling patterns that contain little total mass. The first six modes (and their N_2O content) are 110 years (1025 kg), 3.1 years (2 kg), 2.0 years (-34 kg), 0.68 year (-2 kg), 0.66 year (1 kg), and 0.60 year (9 kg). The modes with negative content are an important part of the complete solution: They are masked by the positive-content modes, and at all altitudes the N_2O mixing ratio remains positive. Note that the negative amount of N_2O associated with the 2.0-year mode actually enhances the apparent perturbation of the primary mode by 2.5%. The perturbation to O_3 has important terms in all six modes as well as many of the short-lived modes with time scales of 0.3 year or less. Thus, on the basis of this model, one would predict that the atmosphere's response to addition of N_2O is complex over the first several years but rapidly converges to the primary mode's pattern of N_2O , NO_y , and O_3 (R3 in Fig. 3). What if the N_2O is emitted in the stratosphere? Much of the nitrous oxide would be destroyed before it reached the troposphere, and indeed, of 1000 kg released at 40 km, only 22 kg goes into the primary mode.

An important lesson from using these modes to represent perturbations to atmospheric chemistry is that almost any change will excite the long-lived modes. For example, addition of atmospheric CO (lifetime of a few months) will induce a substantial perturbation to CH_4 that lasts a couple of decades (2, 13). Using this model we can look at the effect of transient phenomena on the N_2O budget. An instantaneous loss of stratospheric O_3 , for example, 1 DU (1 DU = 10^{-3} cm-atm) globally above 28 km, which is typical of large solar proton events (14), would appear to be repaired in days on the basis of the local chemical time scales for O_3 . Yet this single event would also perturb the century-scale mode of the coup-

Fig. 3. The primary (longest lived) natural mode of the coupled $\{\text{N}_2\text{O}, \text{NO}_y, \text{O}_3\}$ -system expressed as a perturbation (percent change) to the steady-state concentrations of N_2O (circles), NO_y (squares), and O_3 (triangles). The mode is scaled to give a +10% change in N_2O at the surface. The mean steady-state lifetime due



to forcing by surface emissions is 127 years. The four primary modes are as follows: (i) local chemistry and transport only (R0: 125 years); (ii) the same as (i) plus radiative feedback from changing O_3 on the N_2O loss (R1: 107 years); (iii) the same as (i) with radiative feedback on both N_2O and NO_y (R2: 98 years); and (iv) the same as (i) with complete radiative feedback including O_3 self-healing (R3: 110 years).

led system, leaving behind a deficit of N_2O , equivalent to 0.0013 Tg of N emitted at the surface.

The rise in atmospheric N_2O over the last century, presumably due to human activities such as the use of fixed nitrogen in fertilizers (6), has changed the atmosphere and the budget of N_2O . The photochemical coupling of the $\{N_2O, NO_y, O_3\}$ -system that makes perturbations to N_2O decay faster than the steady-state loss rate also implies that the N_2O increase from 275 to 310 ppbv has increased the overall loss rate, reducing the steady-state lifetime by about 1%. The more recent ozone depletion due to chlorofluorocarbons has led to similar offsets in the cumulative N_2O budget (15). On the basis of these results, the offset is small, meaning that we have consistently underestimated the anthropogenic sources of N_2O , but by only a few tenths of a teragram out of 5 TgN/year (8). More accurate estimates of this shift in the N_2O budget, and also of the latitudinal and seasonal patterns of the primary mode, need to be made from numerical experiments with the best current 2D and 3D global atmospheric chemistry models.

In summary, photochemical coupling of N_2O , NO_y , and O_3 in the stratosphere leads to a natural mode for coupled perturbations to all three species that decays 10 to 15% faster than implied from the N_2O steady-state lifetime. This pattern will be excited by emissions of N_2O or by almost any chemical perturbation, for example, those affecting stratospheric ozone. Such coupled patterns might be discernible in the atmosphere. Considering the times scales and strength of chemical coupling among the major atmospheric trace gases, this $\{N_2O, NO_y, O_3\}$ -mode is probably the longest lived perturbation of any significance to the chemical composition of the stratosphere and troposphere.

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The Role of Ocean-Atmosphere Interactions in Tropical Cooling During the Last Glacial Maximum

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A simulation with a coupled atmosphere-ocean general circulation model configured for the Last Glacial Maximum delivered a tropical climate that is much cooler than that produced by atmosphere-only models. The main reason is a decrease in tropical sea surface temperatures, up to 6°C in the western tropical Pacific, which occurs because of two processes. The trade winds induce equatorial upwelling and zonal advection of cold water that further intensify the trade winds, and an exchange of water occurs between the tropical and extratropical Pacific in which the poleward surface flow is balanced by equatorward flow of cold water in the thermocline. Simulated tropical temperature depressions are of the same magnitude as those that have been proposed from recent proxy data.

Although the CLIMAP project (Climate: Long-Range Investigation, Mapping, and Prediction) (1) estimated that, during the Last Glacial Maximum (LGM), tropical temperatures were only modestly lower than they are today, a growing body of evidence, including corals from Barbados (2), ground water from Brazil (3), inferred snow line depressions (4), and ice cores from Peru (5), indicates that the tropics were considerably cooler. There nonetheless continues to be a debate about the extent of this cooling over the low-latitude oceans (rather than land) because some oceanic data are consistent with the CLIMAP results (6).

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Simulations of LGM conditions by means of atmospheric general circulation models reproduce tropical sea surface temperatures (SSTs) that are generally consistent with the CLIMAP results. However, these models neglect oceanic motion that can affect SST. In some of the simulations (4, 7, 8), the SST is specified; in others (9, 10), the ocean is allowed only vertical mixing. Such approximations neglect oceanic upwelling, horizontal advection, and the dynamical ocean-atmosphere interactions that profoundly affect SST and that are of central importance in the following three processes: (i) Tropical ocean-atmosphere interactions of the type that causes the interannual Southern Oscillation between complementary El Niño and La Niña states (11). These interactions involve a positive feedback between the SST and the winds that causes both to amplify or attenuate. Eolian deposits and analyses of planktonic foraminifera (12–14), which indicate that