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Coupling of Nitrous Oxide and Methane by Global Atmospheric Chemistry

Michael J. Prather and Juno Hsu

Nitrous oxide (N\textsubscript{2}O) and methane (CH\textsubscript{4}) are chemically reactive greenhouse gases with well-documented atmospheric concentration increases that are attributable to anthropogenic activities. We quantified the link between N\textsubscript{2}O and CH\textsubscript{4} emissions through the coupled chemistries of the stratosphere and troposphere. Specifically, we simulated the coupled perturbations of increased N\textsubscript{2}O abundance, leading to stratospheric ozone (O\textsubscript{3}) depletion, altered solar ultraviolet radiation, altered stratosphere-to-troposphere O\textsubscript{3} flux, increased tropospheric hydroxyl radical concentration, and finally lower concentrations of CH\textsubscript{4}. The ratio of CH\textsubscript{4} per N\textsubscript{2}O change, –36% by mole fraction, offsets a fraction of the greenhouse effect attributable to N\textsubscript{2}O emissions. These CH\textsubscript{4} decreases are tied to the 108-year chemical mode of N\textsubscript{2}O, which is nine times longer than the residence time of direct CH\textsubscript{4} emissions.

Methane (CH\textsubscript{4}) has environmental impacts beyond those of a direct greenhouse gas, through atmospheric chemistry that enhances the abundance of tropospheric ozone (O\textsubscript{3}) and decreases that of hydroxyl radicals (OH) and hence the atmospheric lifetime of many other pollutants (1, 2). Likewise, nitrous oxide (N\textsubscript{2}O) is a known O\textsubscript{3}-depleting substance (3, 4). Both CH\textsubscript{4} and N\textsubscript{2}O interact directly in the chemistry of stratospheric O\textsubscript{3}, where global CH\textsubscript{4} concentration increases drive proportional but much smaller N\textsubscript{2}O increases (5). The pathway of how N\textsubscript{2}O affects global CH\textsubscript{4} is more complex, involving the coupling of stratospheric O\textsubscript{3} depletion with global tropospheric chemistry through OH, and consequently the lifetime of CH\textsubscript{4}.

This chemical coupling of the stratosphere and troposphere alters one’s expectations about the amplitude and persistence of anthropogenic perturbations. Here we describe four multidecade numerical simulation experiments—one control and three perturbations runs—which have been designed to find such coupling between N\textsubscript{2}O and CH\textsubscript{4} through analysis of long-lived chemical modes. We define modes as the perturbation patterns in the abundances of all chemical species resulting from, for example, the addition of one species (i.e., eigenvectors of the linearized system). In atmospheric chemistry, the most important modes are the long-lived, slowly decaying ones associated with N\textsubscript{2}O and CH\textsubscript{4}, because these have the largest environmental impacts.

The University of California Irvine’s three-dimensional chemistry-transport model incorporates algorithms for both stratospheric and tropospheric chemistry (5–7). The meteorology and trace gas emissions in this study are representative of conditions in the year 2005 (7). For our control run, the CH\textsubscript{4} and N\textsubscript{2}O emissions are prescribed to achieve steady-state abundances of 1775 and 320 parts per billion (ppb), respectively. The annual budgets for N\textsubscript{2}O, CH\textsubscript{4}, and carbon monoxide (CO) from year 80 of this run are summarized in Table 1. Surface N\textsubscript{2}O emissions of 13 Tg of N/year are matched by stratospheric loss. There are small

| Table 1. | Annual mean chemical budget terms (in teragrams/year) and budget lifetimes. Surface emissions, production (prod), and loss are in teragrams/year, except for N\textsubscript{2}O, which are in teragrams of N/year. Terms are split into stratosphere (strat) and troposphere (trop). CO surface deposition is included in trop loss. CH\textsubscript{4} surface deposition is not included, and it would have shortened the CH\textsubscript{4} lifetime to 7.4 years, which is still within the standard deviation of models in (8). 8.7 ± 1.3 years. |
|----------|-----------------------------------------------|----------------|----------------|----------------|----------------|-------|
| Species  | Surface | Trop prod | Trop loss | Strat prod | Strat loss | Lifetime (years) |
| N\textsubscript{2}O | +13.0 | 0 | -0.14 | +0.14 | -13.1 | 118.3 |
| CH\textsubscript{4} | +643 | 0 | -611 | 0 | -32 | 7.8 |
| CO | +1050 | +2070 | -2955 | 0 | -165 | 0.33 |

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CH4 perturbation parallels that of N2O in mode 1. Within the first year, and within two decades, the overall negative perturbation of CH4 appears within the first year, and within two decades, the CH4 perturbation parallels that of N2O in mode 1.

This study looks at the coupled chemistry of stratosphere and troposphere, and thus we examine the mode patterns in Fig. 2 to trace causality, beginning with a surface increase in N2O of 10% (32 ppb). The increase in N2O directly causes an increase in NOy, which depletes O3 by about 2% in the middle stratosphere (a height of 25 to 40 km). The decrease in O3 allows greater penetration of solar ultraviolet (UV) into the middle stratosphere, enhancing the destruction of N2O. Thus, the relative perturbation of N2O declines from +10% to about +8.5% above 35 km. The relative increase in NOy is about the same as that in its source (N2O) below 30 km, but rapidly falls off aloft where the quadratic photochemical loss of NOy buffers its abundance. The maximum decrease of -1.2% in the overhead O3 column occurs at about 22 km and varies with latitude. Lower overhead O3 inventories allow more UV into the lower stratosphere and upper troposphere, where enhanced photolysis of O2 (11) increases O3 by as much as +1.3%. The stratosphere-to-troposphere flux of O3 [-500 Tg/year in this simulation (12, 13)] increases by +0.9%, caused by O3 increases in the mid-latitude lower stratosphere. The O3 column near the surface is reduced by -0.45%, and thus reductions in lower tropospheric O3 concentrations of about -0.2% are driven by increased UV and more rapid photochemical O3 loss under moist conditions [O(3D) + H2O, HO2 + O3].

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The use of chemical modes to deconstruct such perturbations allows for better understanding and predictions. Here we go beyond a one-dimensional (1D) representation of the N2O chemical modes (14) by following the perturbations into 3D tropospheric chemistry. A relatively large reduction in CH4 concentration (3.6 ppb) is tied to an increase in N2O (+10 ppb) that decays with a 108-year time scale. Thus, N2O’s climate impact through radiative forcing is diminished: (i) -8.4% because the decay of a pulse is faster than the e-fold of the steady-state lifetime used previously (15), and (ii) a further -4.5% to account for the decrease in the concentration of CH4. For CH4, the chemical feedbacks are opposite, lengthening the time scale of perturbations and increasing the greenhouse impact by about +40% (16–18).

Using the mode 1 coupling across species, one can readily compute that the N2O concentration increase since preindustrial times, from 270 to 320 Tg, has caused a 2–Dobson unit (DU) (0.7%) decrease in total O3 abundance, as compared with the 3.5% decrease since 1980 that is attributable primarily to halocarbons (19). The corresponding mode 1 offset in CH4 since preindustrial times, -18 ppb, is small relative to the overall CH4 concentration increase of 1000 ppb.

The agreed-on atmospheric residence time for CH4 used to weight emissions in international treaties is based on the mode 2 time scale, currently estimated as 12 years (20). Our derived mode 2 time scale of 12.5 years is well within the uncertainty, but the ratio of residence to budget lifetime in our model is 1.6, at the upper end of the model range in that assessment. Our model thus predicts much stronger chemical feedbacks from CH4 perturbations. The increase in global tropospheric O3 per unit of increase in CH4 is part of the mode 2 pattern calculated here, and the ratio in more traditional units, 3.1 DU/ppm, is similar to other model results (for example, 3.7 for (2) and 2.4 for (11)). The CO-CH4 coupling here, 7.4 Tg of CH4 generated from 100 Tg of CO, is consistent with the indirect global warming potential of CO emissions (18).
Table 2. Chemical modes and amplitudes excited by pulses of N\textsubscript{2}O, CO, and CH\textsubscript{4}. The modes are identified with perturbation minus control (P – C) simulations. Amplitudes (A) are in globally integrated teragrams of N for N\textsubscript{2}O and NO\textsubscript{y} and in teragrams for other species. The amplitudes of these modes are characterized by the amounts of N\textsubscript{2}O (mode 1) and CH\textsubscript{4} (mode 2), shown in bold. Relative small amplitudes are not shown (–).

|     | Initial pulse | Mode (time) | A \textsubscript{N\textsubscript{2}O} | A NO\textsubscript{y} | A CH\textsubscript{4} | A O\textsubscript{3} | A trop O\textsubscript{3} |
|-----|---------------|-------------|--------------------------------------|----------------------|---------------------|---------------------|--------------------------|
| C2–C1 | 10 Tg of N from N\textsubscript{2}O | 1 (108.4 years) | +10.2                               | +0.011               | –2.1                | –0.93               | –0.01                    |
|      |               | 2 (12.5 years) | –0.002                               | +2.8                 | +0.11               | 0.03                |                          |
| C3–C1 | 100 Tg of CO   | 1 (108.4 years) | +0.0045                              | –0.00003             | +7.4                | +0.30               | +0.09                    |
|      |               | 2 (12.5 years) | +0.006                               | –0.00004             | +9.85               | +0.40               | +0.12                    |

This N\textsubscript{2}O-CH\textsubscript{4} coupling will shift with climate change over the 21st century. For example, the upper stratosphere cools as CO\textsubscript{2} increases, and this temperature change alters the N\textsubscript{2}O-NO\textsubscript{y}-O\textsubscript{3} chemistry, reducing the impact of N\textsubscript{2}O on O\textsubscript{3} (27). The importance of N\textsubscript{2}O as an ozone-depleting substance (22) will thus be reduced, weakening the coupling described here but still maintaining the negative greenhouse feedback effect of CH\textsubscript{4} on N\textsubscript{2}O emissions.

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Fossil Evidence for Evolution of the Shape and Color of Penguin Feathers

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Penguin feathers are highly modified in form and function, but there have been no fossils to inform their evolution. A giant penguin with feathers was recovered from the late Eocene (~36 million years ago) of Peru. The fossil reveals that key feathering features, including undifferentiated primary wing feathers and broad body contour feather shafts, evolved early in the penguin lineage. Analyses of fossilized color-imparting melanosomes reveal that their dimensions were similar to those of non-penguin avian taxa and that the feathering may have been predominantly gray and reddish-brown. In contrast, the dark black-brown color of extant penguin feathers is generated by large, ellipsoidal melanosomes previously unknown for birds. The nanostructure of penguin feathers was thus modified after earlier macrostructural modifications of feather shape linked to aquatic flight.

During wing-propelled diving, penguins generate propulsive forces in a fluid environment ~800 times more dense and ~70 times more viscous than air (1). Recent fossil discoveries have yielded information on the sequence of early osteological changes in penguins accompanying the evolution of aquatic flight (2–5), but these specimens have not included feathers. Living penguin melanosome morphologies have been described, although the melan in them contain is generally known to provide both color and wear resistance to bird feathers (6–8). Here, we describe a giant fossil penguin with feathers recording preserved melanosome morphologies (9) and discuss the pattern and timing of major events in the evolution of penguin integument.

Systematic paleontology: Aves Linnaeus 1758 sensu Gauthier 1986. Sphenisciformes Sharpe 1891 sensu Clarke et al. 2003. Inkayacu paraacasensis new gen. and sp. Etymology: Inkayacu—the Quechua, “Inka” for emperor and “yacu” for water; paraacasensis for the Reserve Nacional de Paracas, Peru, the type locality.

Holotype: MUSM 1444, a nearly complete skeleton with wing feathering, body contour feathers, and pedal scales (Figs. 1 to 3) (10). Locality and horizon: Upper Eocene of Yumacque Point, Paracas Reserve, Peru (10). Diagnosis: Inkayacu paraacasensis is diagnosed by the following combination of characters (autapomorphies within Sphenisciformes demarcated by an asterisk): paired grooves meeting at midline on dorsal surface of premaxilla* (Fig. 1, GR), articular surfaces of otic and squamosal head of quadrate contacting one another,* furcula with blade-like hypolepidium,* conspicuous n. coracobrachialis sulcus developed on the humerus (Fig. 1, CNS), femur with widened and sharply distally tapering medial condyle* and tab-like process projecting from posterior intramuscular ridge at midshaft* (Fig. 1, MC and T), and weak proximal projection of crural crests of tibiotarsus (Fig. 1, CNE). See (10) for additional diagnosis, figures, and description.