Coupling of nitrous oxide and methane by global atmospheric chemistry

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Coupling of Nitrous Oxide and Methane by Global Atmospheric Chemistry

Michael J. Prather and Juno Hsu

Nitrous oxide (N$_2$O) and methane (CH$_4$) are chemically reactive greenhouse gases with well-documented atmospheric concentration increases that are attributable to anthropogenic activities. We quantified the link between N$_2$O and CH$_4$ emissions through the coupled chemistries of the stratosphere and troposphere. Specifically, we simulated the coupled perturbations of increased N$_2$O abundance, leading to stratospheric ozone (O$_3$) depletion, altered solar ultraviolet radiation, altered stratosphere-to-troposphere O$_3$ flux, increased tropospheric hydroxyl radical concentration, and finally lower concentrations of CH$_4$. The ratio of CH$_4$ per N$_2$O change, $-36\%$ by mole fraction, offsets a fraction of the greenhouse effect attributable to N$_2$O emissions. These CH$_4$ decreases are tied to the 108-year chemical mode of N$_2$O, which is nine times longer than the residence time of direct CH$_4$ emissions.

Methane (CH$_4$) has environmental impacts beyond those of a direct greenhouse gas, through atmospheric chemistry that enhances the abundance of tropospheric ozone (O$_3$) and decreases that of hydroxyl radicals (OH) and hence the atmospheric lifetime of many other pollutants (1, 2). Likewise, nitrous oxide (N$_2$O) is a known O$_3$-depleting substance (3, 4). Both CH$_4$ and N$_2$O interact directly in the chemistry of stratospheric O$_3$, where global CH$_4$ concentration increases drive proportional but much smaller N$_2$O increases (5). The pathway of how N$_2$O affects global CH$_4$ is more complex, involving the coupling of stratospheric O$_3$ depletion with global tropospheric chemistry through OH, and consequently the lifetime of CH$_4$.

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$_2$O and CH$_4$ through analysis of long-lived chemical modes. We define modes as the perturbation patterns of 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$_2$O and CH$_4$, 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$_4$ and N$_2$O emissions are prescribed to achieve steady-state abundances of 1775 and 320 parts per billion (ppb), respectively. The annual budgets for N$_2$O, CH$_4$, and carbon monoxide (CO) from year 80 of this run are summarized in Table 1. Surface N$_2$O emissions of 13 Tg of N/year are matched by stratospheric loss. There are small

<table>
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<th>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$_2$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$_4$ surface deposition is not included, and it would have shortened the CH$_4$ lifetime to 7.44 years, which is still within the standard deviation of models in (8). 8.7 ± 1.3 years.</th>
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<tbody>
<tr>
<td><strong>Species</strong></td>
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<tr>
<td>N$_2$O</td>
</tr>
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<td>CH$_4$</td>
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<td>CO</td>
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destruction. Thus, the avoided loss, about 0.2 Tg of N, adds to the amplitude of mode 1, amplifying the integrated radiative forcing from the N₂O pulse. Such an increase of about 2% should be applied to all greenhouse gases with stratospheric loss, such as chlorofluorocarbons, but not to those with tropospheric loss, such as hydrofluorocarbons. In a similar but opposite vein, the pulse of 10 Tg of CH₄ (C4) has an amplitude of only 9.85 Tg in mode 2, because the most rapid loss occurs in the lower atmosphere where it is emitted. The N₂O pulse (C2) produces a CH₄ amplitude of −2.1 Tg in mode 1 and +2.8 Tg in mode 2. This pulse must also excite other, short-lived modes (not seen here) with a net CH₄ amplitude of −0.7 Tg, because the initial CH₄ perturbation is zero. 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 (32 ppb). The increase in 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(¹D) + H₂O, HO₂ + O₃]. The global burden of CH₄ is decreased by −0.65% because of greater tropospheric OH abundances, caused by enhanced UV from the smaller O₃ column. Like N₂O, the relative perturbation of CH₄ declines further to −1.5% by 50 km because of the enhanced UV and loss in the middle stratosphere.

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 ppb, 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 per ppm, is similar to other model results [for example, 3.7 for (2) and 2.4 for (1)]. 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).

**Fig. 1.** Decay of atmospheric chemical perturbations caused by an initial pulse of (A) 10 Tg of N from N₂O and (B) 100 Tg of CO (1 Tg = 10⁹ kg). Perturbations represent the total atmospheric burden of key species. Positive perturbations are indicated by solid lines; negative ones by dashed lines. The asymptotic behavior in (A) is chemical mode 1 with a decay time of 108 years. (B) shows both mode 2 (12.5 years) and mode 1 (N₂O only) decays. Values are plotted every 1 January, beginning 1 year after the initial pulse. The thin extension lines in (B) for O₃ (total) and CO indicate difficulties in separating the modes in both control C1 and perturbation C3.

**Fig. 2.** Altitude profiles of the pattern of key species in mode 1 on 1 January. For N₂O, NOy, and CH₄, each profile is a global mean, but for O₃ the profiles are sampled at the equator and 40°N latitude. The amplitudes are shown as relative to the steady-state profiles and are scaled to 10% in N₂O at the surface.
This N₂O-CH₄ coupling will shift with climate change over the 21st century. For example, the upper stratosphere cools as CO₂ increases, and this temperature change alters the N₂O-N₂O₃-O₃ chemistry, reducing the impact of N₂O on O₃ (21). The importance of N₂O as an ozone-depleting substance (22) will thus be reduced, weakening the coupling described here but still maintaining the negative greenhouse feedback effect of CH₄ on N₂O emissions.

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 not been described, although the melanin they 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.

**Table 2.** Chemical modes and amplitudes excited by pulses of N₂O, CO₂, and CH₄. The modes are identified with perturbation minus control (P – C) simulations. Amplitudes (A) are in globally integrated teragrams of N for N₂O and NO₃ and in teragrams for other species. The amplitudes of these modes are characterized by the amounts of N₂O (mode 1) and CH₄ (mode 2), shown in bold. Relatively small amplitudes are not shown (–).

<table>
<thead>
<tr>
<th>P – C</th>
<th>Initial pulse</th>
<th>Mode (time)</th>
<th>A N₂O</th>
<th>A NO₃</th>
<th>A CH₄</th>
<th>A O₃</th>
<th>A trop O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 – C1</td>
<td>10 Tg of N from N₂O</td>
<td>1 (108.4 years)</td>
<td>+10.2</td>
<td>+0.011</td>
<td>–2.1</td>
<td>–0.93</td>
<td>–0.01</td>
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<tr>
<td></td>
<td></td>
<td>2 (12.5 years)</td>
<td>–0.002</td>
<td>–2.8</td>
<td>+0.11</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>C3 – C1</td>
<td>100 Tg of CO</td>
<td>1 (108.4 years)</td>
<td>+0.0045</td>
<td>–0.00003</td>
<td>+7.4</td>
<td>+0.30</td>
<td>+0.09</td>
</tr>
<tr>
<td>C4 – C1</td>
<td>10 Tg of CH₄</td>
<td>1 (108.4 years)</td>
<td>+0.006</td>
<td>–0.00004</td>
<td>+9.85</td>
<td>+0.40</td>
<td>+0.12</td>
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<tr>
<td></td>
<td></td>
<td>2 (12.5 years)</td>
<td>–0.007</td>
<td>–0.00004</td>
<td>+9.85</td>
<td>+0.40</td>
<td>+0.12</td>
</tr>
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References and Notes

7. Materials and methods are available as supporting material on Science Online.
23. This research was supported by NSF’s Atmospheric Chemistry program (grant ATM050234) and NASA’s Modeling, Analysis, and Prediction/Glbal Modeling Initiative program (grants NN06G684G and NN09A947G).

Supporting Online Material

www.sciencemag.org/cgi/content/full/330/6006/952/DC1

Methods

References

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