

# Indirect long-term global radiative cooling from $\text{NO}_x$ emissions

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**Abstract.** Anthropogenic emissions of short-lived, chemically reactive gases, such as  $\text{NO}_x$  and  $\text{CO}$ , are known to influence climate by altering the chemistry of the global troposphere and thereby the abundance of the greenhouse gases  $\text{O}_3$ ,  $\text{CH}_4$  and the HFCs. This study uses the characteristics of the natural modes of the tropospheric chemical system to decompose the greenhouse effect of  $\text{NO}_x$  and  $\text{CO}$  emissions into (i) short-lived modes involving predominantly tropospheric  $\text{O}_3$  and (ii) the long-lived mode involving a global coupled  $\text{CH}_4$ - $\text{CO}$ - $\text{O}_3$  perturbation. Combining these two classes of greenhouse perturbations—large, short-lived, regional  $\text{O}_3$  increases and smaller, long-lived, global decreases in  $\text{CH}_4$  and  $\text{O}_3$ —we find that most types of anthropogenic  $\text{NO}_x$  emissions lead to a negative radiative forcing and an overall cooling of the earth.

## 1. Introduction

The direct radiative forcing (RF) of the greenhouse gases  $\text{CH}_4$ ,  $\text{O}_3$  and the HFCs has been the subject of numerous studies, and has been reviewed in recent assessment reports [Schimel *et al.*, 1996; Granier and Shine, 1999]. However, the chemical lifetime of many of these species in the troposphere is strongly influenced by short-lived gases with little or no radiative effects in the wavelength range important for climate. The ‘indirect’ climate effects of these reactive species have been shown to make a significant contribution to the total RF [Hauglustaine *et al.*, 1994; Johnson and Derwent, 1996; Fuglestedt *et al.*, 1996; Daniel and Solomon, 1998], but detailed quantification of the effects has proved difficult due in part to the wide range of temporal and spatial scales involved.

This paper presents a new method of quantifying these effects using the natural modes of the tropospheric chemical system. The technique allows the full, time-integrated impacts of emissions changes to be assessed, including the effects of temporal and spatial variations, but without the need for decades-long model runs. We apply the technique to  $\text{NO}_x$  emissions from a variety of sources, and demonstrate that currently incremental increases in anthropogenic  $\text{NO}_x$

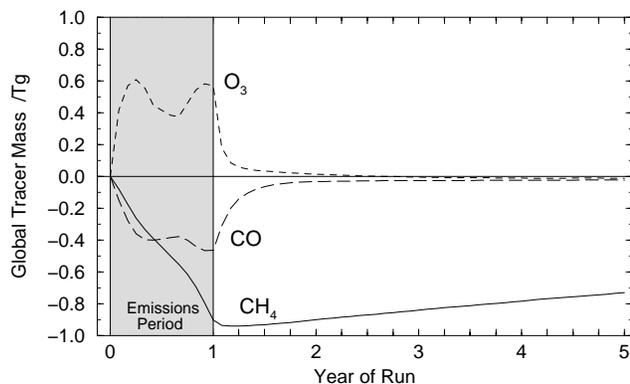
emissions have a negative integrated RF. In this case long-term cooling due to decreases in  $\text{CH}_4$  and  $\text{O}_3$  dominates short-term warming from regional  $\text{O}_3$  increases.

## 2. Excitation of the Primary Mode

The coupling of chemical processes with atmospheric transport leads to the existence of natural modes in the tropospheric system which describe how chemical species co-vary in space and time through the different chemical environments present in the atmosphere. The modes correspond to the eigenstates of the chemical system, and each has a characteristic time-scale corresponding to the respective eigenvalue of the system [Prather, 1994, 1996]. In previous work [Wild and Prather, 2000], we demonstrated the structure and behaviour of these global chemical modes using a tropospheric Chemical Transport Model (CTM) and showed how the primary natural mode, describing the  $\text{CH}_4$ - $\text{CO}$ - $\text{OH}$  coupling, could be excited by regional emissions of short-lived species. This mode, with a decay time about 50% longer than the chemical lifetime of  $\text{CH}_4$ , dominates the long-term radiative impacts of most tropospheric perturbations.

These studies are performed using the University of California, Irvine (UCI) CTM described in earlier work [Wild and Prather, 2000]. The model is run using a single year of meteorological fields from the GISS II' GCM [Rind and Lerner, 1996] at  $4^\circ \times 5^\circ$  resolution. The CTM resolution is degraded to  $8^\circ \times 10^\circ$  to reduce computational costs, and the fields are recycled for the multiple-year runs needed here. The model includes a detailed tropospheric chemistry scheme with hydrocarbon oxidation and the effects of stratospheric chemistry via first-order rates of change above a tracer-diagnosed tropopause. Emissions data for 1985 are used, and are described in the previous study.

The CTM is initialized and run for 10 years with fixed emissions to provide a control. The perturbation runs are initialized likewise and run for 10 years but with emissions from particular sources increased by a factor for the first year and returning to the standard emissions for years 2 to 10. The differences between perturbation and control runs are used to integrate the short-lived perturbations to tropospheric  $\text{O}_3$  and  $\text{CH}_4$  and to determine the asymptotic behaviour of the perturbation (i.e., the amplitude of the primary mode). Since the primary mode has an exact  $e$ -fold



**Figure 1.** Evolution of the global mass perturbations of O<sub>3</sub>, CO and CH<sub>4</sub> due to the additional emission of 0.5 TgN of global fossil fuel NO for one year.

decay (with annually recycling meteorology), the long-term integration can be analytically evaluated from the product of the amplitude and the  $e$ -fold time, saving much computational effort over a steady-state CTM calculation that would take several decades to achieve even 10% accuracy. The incremental NO<sub>x</sub> emissions excite the primary mode in a negative sense; CH<sub>4</sub> decreases are paralleled by an increase in OH and a decrease in O<sub>3</sub>, CO, NO<sub>y</sub> and peroxy radicals [Wild and Prather, 2000]. After the transient, regional effects have decayed, perturbations of all species decay with the timescale of the primary mode, 14.2 years in this model. Although we follow the decay of a pulse, the integral of a single year's emissions is equivalent to the steady state that would accumulate from continuous emissions.

### 3. Estimates of Radiative Forcing

The direct RF for CH<sub>4</sub> and O<sub>3</sub> perturbations in the current atmosphere is based on previous studies: +0.37 mW m<sup>-2</sup> ppb<sup>-1</sup> for CH<sub>4</sub> [Schimel et al., 1996] for a constant mixing ratio perturbation through the troposphere, and +42 mW m<sup>-2</sup> per Dobson Unit change in column tropospheric O<sub>3</sub> [D. Hauglustaine, personal communication, 2000]. The RF per unit O<sub>3</sub> depends on region and season [Fuglestedt et al., 1996] and particularly on altitude [Lacis et al., 1990]. While the short-lived perturbations here are regionally driven, the changes in O<sub>3</sub> tend to be dispersed through the mid-troposphere in mid-latitudes and hence may be represented by the mean factor above. The long-lived, primary-mode perturbations are more globally uniform, and hence this simple approach to scaling the RF to the change in total tropospheric O<sub>3</sub> provides a suitable estimate. We adopt an uncertainty of 20%, based on the range of forcings from a recent model intercomparison [Ramaswamy et al., 2001], to account for this effect.

We calculate the time-integrated forcing for the primary mode from the amplitude of excitation and the decay time. For a 1.0 Tg perturbation in CH<sub>4</sub>, 99.3% of the oxidation is accounted for by the primary mode [Wild and Prather, 2000], and hence the integrated perturbation is 14 Tg-yr of CH<sub>4</sub> with an RF of 1.9 mW m<sup>-2</sup> yr. The O<sub>3</sub> perturbation tied to this excitation of the primary mode is 0.016 Tg-yr of O<sub>3</sub> with an integrated RF of about 0.87 mW m<sup>-2</sup> yr, 45% of the magnitude of the CH<sub>4</sub> RF. This long-lived O<sub>3</sub> perturbation occurs whenever the primary mode is excited, although

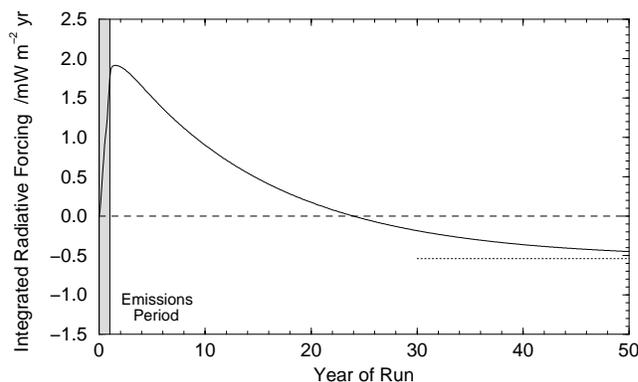
it is often masked initially by large O<sub>3</sub> perturbations present in short-lived modes.

### 4. NO<sub>x</sub> perturbation studies

In Figure 1 we show the evolution of the perturbation in global mass of O<sub>3</sub>, CH<sub>4</sub> and CO for a one-year, 0.5 TgN increment in NO<sub>x</sub> emissions from global fossil fuel sources. The extra NO<sub>x</sub> leads to additional O<sub>3</sub> formation in the region of emissions and to increased OH, exciting the primary mode by increasing oxidation of CH<sub>4</sub> and CO. Immediately following the period of additional NO<sub>x</sub> emissions, the O<sub>3</sub> and CO perturbations associated with short-lived modes decay rapidly with  $e$ -fold times of 2–3 months, but the CH<sub>4</sub> perturbation decays with an  $e$ -fold time of 14.2 years. Two years later, the O<sub>3</sub> perturbation changes sign, as the global decrease associated with the primary mode dominates the short-term regional increases.

The evolution of the integrated RF due to these changes in O<sub>3</sub> and CH<sub>4</sub> is shown in Figure 2. While the initial RF driven by O<sub>3</sub> formation is positive, long-term cooling due to the primary mode gradually reduces this until, after about 24 years, the integrated RF becomes negative and tends to a total net of  $-0.54$  mW m<sup>-2</sup>. The net integrated perturbations and RFs due to NO<sub>x</sub> emissions from a variety of sources are shown in Table 1. Industrial and fossil fuel sources have been subdivided by region to highlight differences in chemical and meteorological environment; while all perturbations follow a pattern similar to that shown in Figure 1, their magnitudes differ greatly, dependent on the O<sub>3</sub> production efficiency of the added NO<sub>x</sub> and on the additional OH formation. For aircraft emissions, predominantly in the upper troposphere at northern mid-latitudes, the additional O<sub>3</sub> dominates the CH<sub>4</sub> removal and leads to net radiative warming. The effects are proportional to, but slightly lower than, those derived in the recent IPCC Aircraft Assessment [Penner et al., 1999] ( $-15$  mW m<sup>-2</sup> for CH<sub>4</sub>,  $+24$  mW m<sup>-2</sup> for O<sub>3</sub>). For lightning emissions, principally in tropical regions, the perturbation to OH and hence CH<sub>4</sub> is larger per unit NO<sub>x</sub> emission and dominates the warming due to O<sub>3</sub>. This reduces the likelihood of positive climate feedbacks between O<sub>3</sub> and lightning [Toumi et al., 1996].

For all surface emissions studied here, the primary mode dominates the RF, with a small net cooling in each case.



**Figure 2.** Evolution of the integrated radiative forcing due to changes in CH<sub>4</sub> and O<sub>3</sub> caused by the additional emission of 0.5 TgN of global fossil fuel NO for one year.

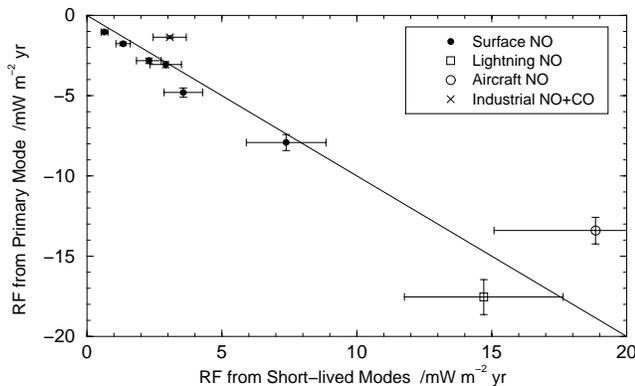
**Table 1.** Integrated perturbations to CH<sub>4</sub> and tropospheric O<sub>3</sub> (Tg-yr) and their estimated radiative forcing (RF: W m<sup>-2</sup> yr) due to a 0.5 TgN increase in emissions for one year.

Perturbation	ΔCH <sub>4</sub>	ΔO <sub>3</sub>	ΔO <sub>3</sub> (Tg-yr) <sup>a</sup>		R.F. (mW m <sup>-2</sup> yr)		
	Total (Tg-yr)	Total (Tg-yr)	Short-lived Modes	Primary Mode	ΔCH <sub>4</sub>	ΔO <sub>3</sub>	Net
Aircraft NO	-67.1	3.79	4.91	-1.11	-9.1	14.6	5.4
Lightning NO	-87.8	2.37	3.83	-1.46	-11.9	9.1	-2.8
Biomass Burning NO	-24.1	0.53	0.93	-0.40	-3.3	2.0	-1.2
Industrial NO	-14.2	0.36	0.59	-0.23	-1.9	1.4	-0.5
— Europe	-5.2	0.08	0.17	-0.09	-0.7	0.3	-0.4
— N.America	-8.9	0.20	0.34	-0.15	-1.2	0.8	-0.4
— E.Asia	-15.4	0.50	0.76	-0.26	-2.1	1.9	-0.2
— Tropics	-39.6	1.26	1.92	-0.66	-5.4	4.9	-0.5
Industrial NO and CO <sup>b</sup>	-6.8	0.68	0.79	-0.11	-0.9	2.6	1.7

<sup>a</sup>The O<sub>3</sub> perturbation is split into contributions from the short-lived modes and the long-lived primary mode.

<sup>b</sup>Includes also CO emissions (10 Tg CO for one year).

For CH<sub>4</sub>, the long-term integrated RF per increment in annual NO<sub>x</sub> emissions ranges from -1.4 to -10.8 mW m<sup>-2</sup> per TgN/yr, similar to the -5 mW m<sup>-2</sup> found by *Fuglestedt et al.*, [1996] from step increases in continuous emissions. For O<sub>3</sub>, the long-term integrated RF ranges from +0.6 to +9.7 mW m<sup>-2</sup> per TgN/yr. Previous 2-D model studies have suggested +3.1 [*Fuglestedt et al.*, 1996] and +1.4 to +6.4 mW m<sup>-2</sup> [*Johnson and Derwent*, 1996], with strong regional variations. [*Fuglestedt et al.*, 1999] find CH<sub>4</sub> and O<sub>3</sub> RF of -5.0 and +3.5 mW m<sup>-2</sup> per TgN/yr, respectively, from US emissions. We find lower but proportional forcings of -2.4 and +1.6 mW m<sup>-2</sup> for fossil fuel emissions over a similar region. The relationship between the transient response in O<sub>3</sub> associated with short-lived modes and the long-term perturbation in CH<sub>4</sub> associated with the primary mode is shown in Figure 3. With the exception of aircraft emissions (open circle), all scenarios for NO<sub>x</sub> increases fall below the zero-forcing line, indicating a net negative integrated forcing.



**Figure 3.** A scatter plot of the integrated radiative forcing (RF) from CH<sub>4</sub> and O<sub>3</sub> in the primary mode against that of O<sub>3</sub> in short-lived modes for model runs with additional one-year emissions of 0.5 TgN from a variety of sources (see Table 1). Above the zero-forcing line, the warming effects of short-term O<sub>3</sub> increases dominate; below, radiative cooling due to the primary mode dominates. Error bars of 20% are indicated for the RF from O<sub>3</sub>.

In contrast to NO<sub>x</sub>, emissions of CO reduce OH concentrations and therefore excite the primary mode in a positive sense. As NO<sub>x</sub> and CO have similar combustion sources, we consider the impact of coupled emissions by pairing the 0.5 TgN/yr increase in global industrial NO<sub>x</sub> sources with a proportional increase in CO emissions (10 TgCO/yr). The primary mode is still excited in a negative sense but with about half the amplitude of that due to increased NO<sub>x</sub> emissions alone. This highlights the greater sensitivity of OH to NO<sub>x</sub> rather than to CO emissions near the surface. Additional O<sub>3</sub> formation attributable to CO emissions leads to about a third more O<sub>3</sub> in the short-lived modes, and drives the net RF positive for this coupled emission (shown with a cross in Figure 3).

## 5. Conclusions

The identification of RF caused by emission of short-lived, chemically reactive gases with both short-lived and long-lived chemical modes is extremely useful. This separation of the problem can greatly reduce the computational effort for tropospheric chemical modeling, enabling a wide range of sensitivity studies such as the examples here. Further, it provides both insight and a clear quantitative separation of RF that is regional (short-lived modes) from that which is global (the long-lived CH<sub>4</sub>-CO-O<sub>3</sub> mode). Since these two different patterns of radiative forcing may not cancel, even with opposite signs, it may become important to diagnose them separately.

Anthropogenic surface emissions of NO<sub>x</sub> produce a net RF, due to changes in O<sub>3</sub> and CH<sub>4</sub>, that is consistently negative but can vary by an order of magnitude depending on region. Combined industrial emissions of CO and NO<sub>x</sub>, however, yield a positive RF. Thus decisions to control global tropospheric O<sub>3</sub> and hence greenhouse warming by cutting NO<sub>x</sub> emissions alone would produce the opposite effect when the long-term, global changes to both CH<sub>4</sub> and O<sub>3</sub> are considered.

This study has some clear inadequacies. For one, the treatment of urban emissions in the CTM does not include the effects of non-linearities in small-scale plumes where NO<sub>x</sub> concentrations may be sufficiently high to suppress O<sub>3</sub> production or to remove NO<sub>x</sub> rapidly. It is not clear in these

cases that the OH effect is also proportionally suppressed. Uncertainties such as these can be evaluated by comparing the global CTM with carefully designed, high-resolution regional models. Second, the inhomogeneity of the short-term O<sub>3</sub> increases adds uncertainty in estimating its RF that is estimated here to be about  $\pm 20\%$ . Also, we have assumed that RF is additive in terms of climate impact and hence that tropospheric O<sub>3</sub> heating cancels CH<sub>4</sub> cooling. These latter assumptions can only be tested in a climate model.

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