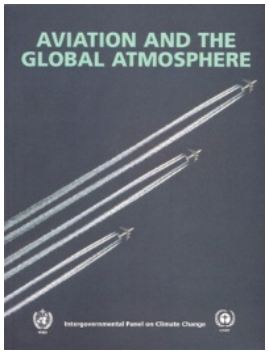
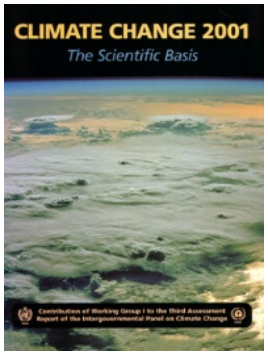


1999



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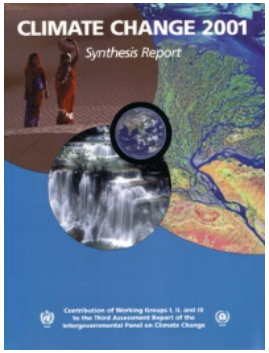

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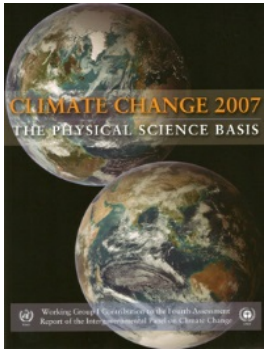

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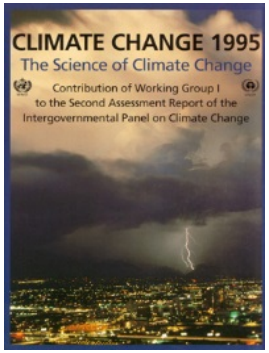
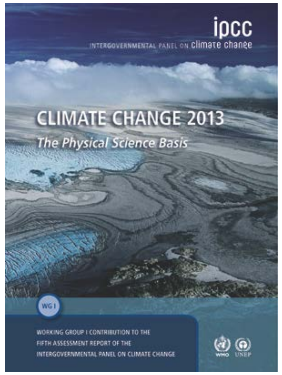


1995

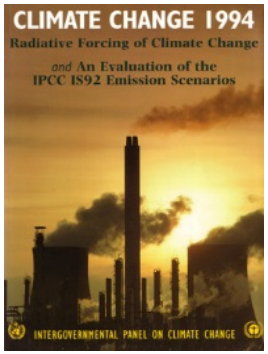
Keeping Atmospheric Chemistry in the IPCC Climate Assessments

Michael Prather
Earth System Science Professor, UC Irvine (1992 -)

A presentation for the Clean Air Leadership Talks.
18 May 2016, Sacramento, CA

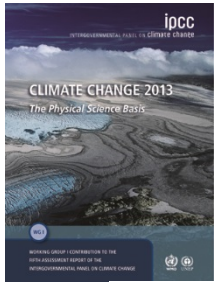


2013



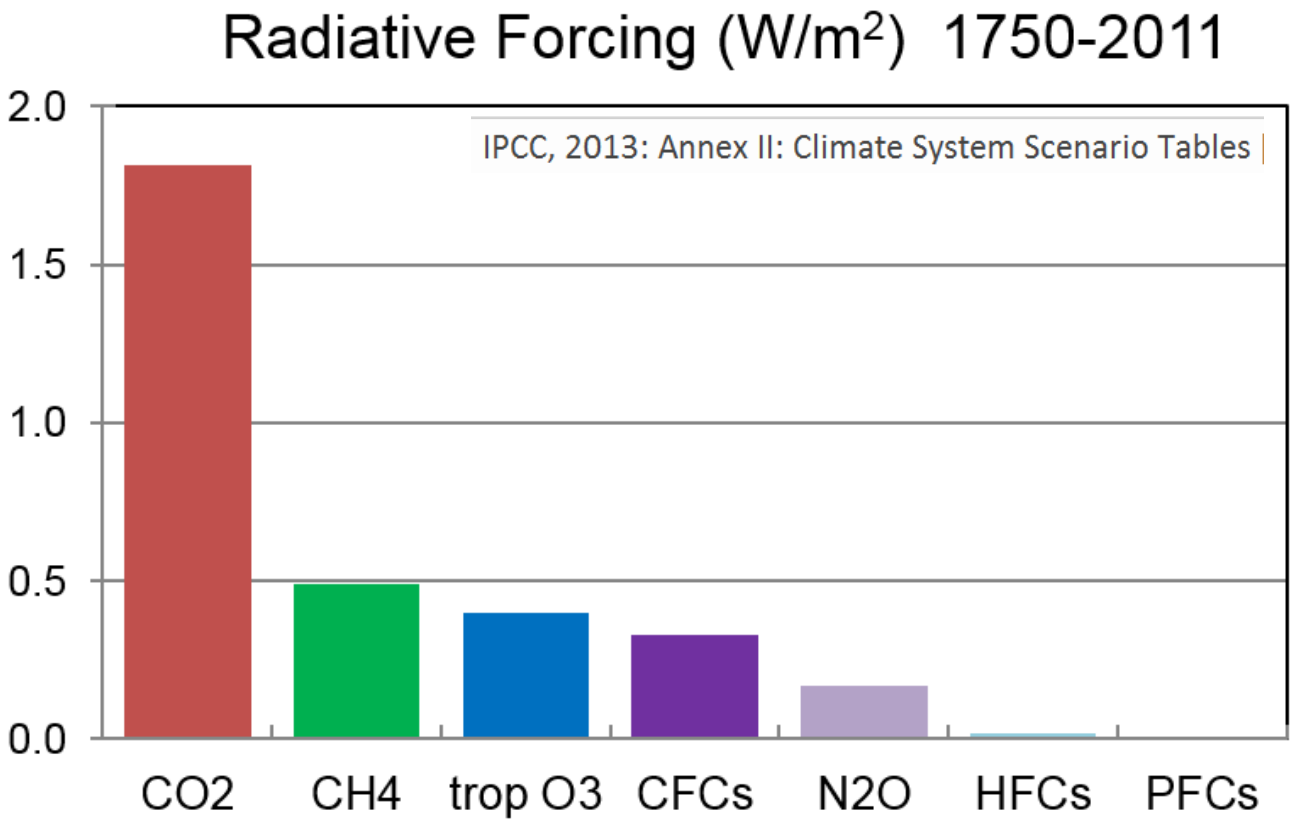
1994

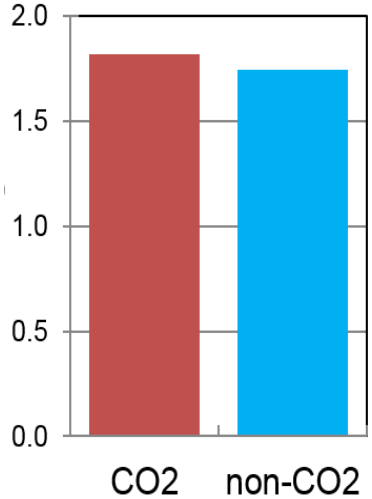
2014



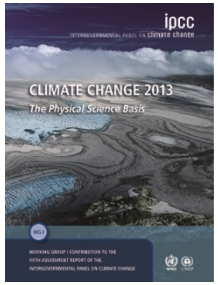
2013

Why do we care about atmospheric chemistry for climate? Is it not all just CO_2?



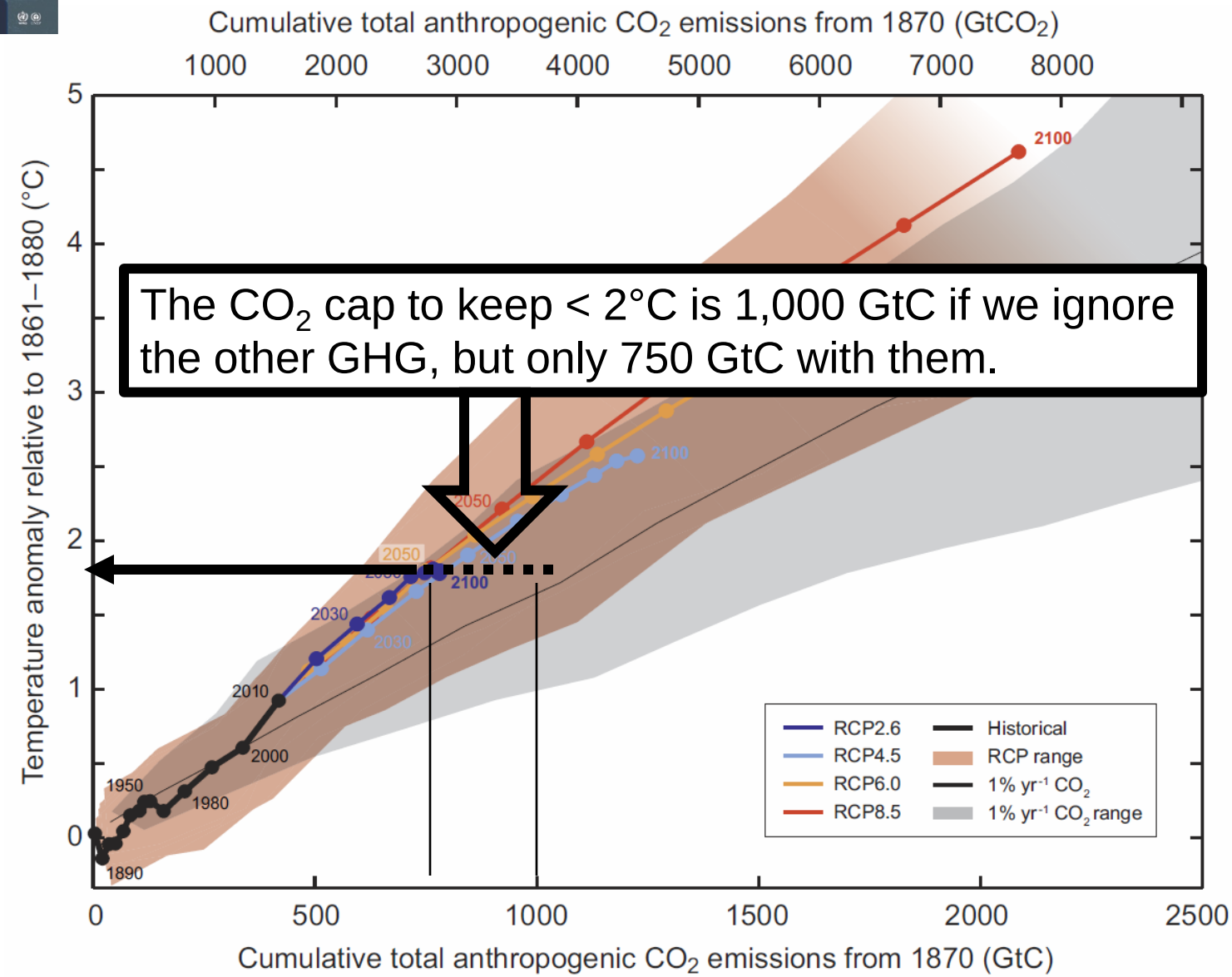


The non-CO_2 gases add up.

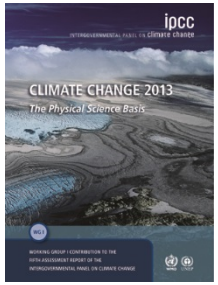


2013

Why do we care about atmospheric chemistry for climate? Is it not all just CO_2?



The CO_2 cap to keep < 2°C is 1,000 GtC if we ignore the other GHG, but only 750 GtC with them.



2013

13 Sea Level Change

Coordinating Lead Authors:
John A. Church (Australia), Peter U. Clark (USA)

The New York Times | http://nyti.ms/1rR213I

AUSTRALIA

Australia to Lay Off Leading Scientist on Sea Levels

By MICHELLE INNIS MAY 17, 2016

SYDNEY — A pre-eminent scientist in the field of rising global sea levels has been given notice of his dismissal as part of deep cuts at Australia's national science agency that will reduce the country's role in global climate research.

The scientist, John Church, confirmed Tuesday that he was one of 275 scientists that the agency, the Commonwealth Scientific and Industrial Research Organization, or Csiro, said would be laid off.

IPCC
the Intergovernmental Panel on Climate Change

Just how did I get involved?

Just how did IPCC redirect my research?

a personal scientific history & reflection

In 1990, while playing with our new 3D chemistry model, we discovered a magic trick for calculating the OH-lifetime of any gas by simple scaling!

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 95, NO. D11, PAGES 18,723–18,729, OCTOBER 20, 1990

Tropospheric OH and the Lifetimes of Hydrochlorofluorocarbons

MICHAEL PRATHER

NASA Goddard Space Flight Center, Institute for Space Studies, New York

CLARISA M. SPIVAKOVSKY

Center for Earth and Planetary Physics, Harvard University, Cambridge, Massachusetts

Hydrochlorofluorocarbons (HCFCs) may be used as alternatives for the chlorofluorocarbons (CFCs). Lifetimes for the HCFCs are predicted here in two ways: integrating their loss with a global model, and scaling to another compound with a better known lifetime. Both approaches are shown here to yield similar results. Three-dimensional fields of modeled tropospheric OH concentrations are used to calculate lifetimes against destruction by OH for the HCFCs and other hydrogenated halocarbons. The OH fields are taken from a three-dimensional chemical transport model [*Spivakovsky et al.*, 1990a] that accurately simulates the global measurements of methyl chloroform (derived lifetime of 5.5 yr). The lifetimes of various hydro-halocarbons are shown to be insensitive to possible spatial variations and seasonal cycles. It is possible to scale the HCFC lifetimes to that of methyl chloroform or methane by using a ratio of the rate coefficients for reaction with OH at an appropriate temperature, about 277 K.

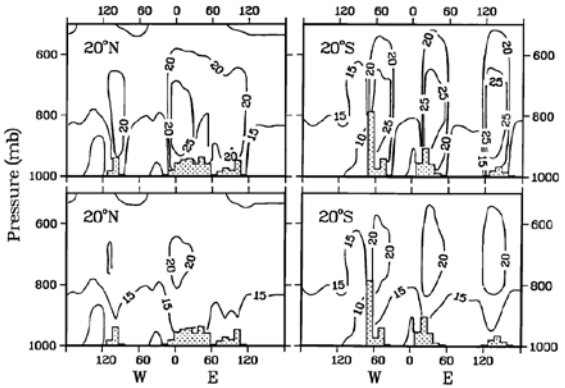
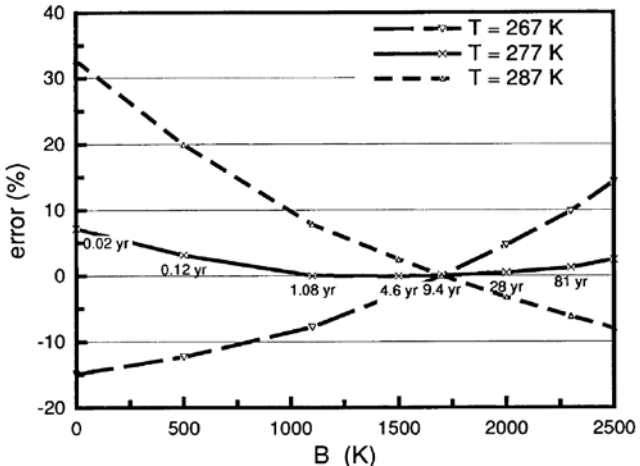


Fig. 2. Contours of tropospheric OH (units: 10^5 molecules cm^{-3}) calculated with the three-dimensional model for two subtropical latitudinal bands 8° wide, centered at 20°. The lower panels show OH concentrations calculated with maximum values of NO_x, CO, and O_3 assumed throughout the globe.

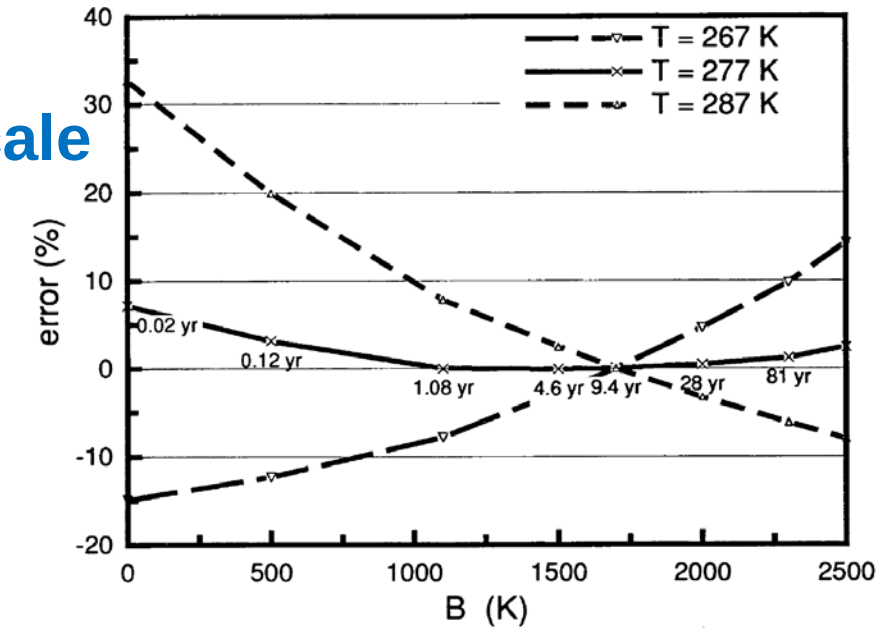


In 1990, while playing with our new 3D chemistry model, we discovered a magic trick for calculating the OH-lifetime of any gas by simple scaling! ***in std use since 1990***

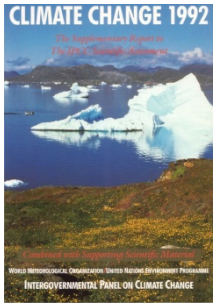
Fig. 1. Error (%) in predicting HCFC lifetimes by scaling the rate coefficient

lifetimes against OH loss scale

as $k_{OH} = A \exp(- B / 277K)$



key knowledge for IPCC ***GWP***s and UNEP/WMO ***ODP***s, which all depend on lifetimes.



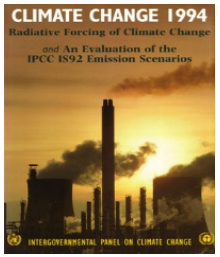
1992

A2.3.6 Indirect GWPs of Well-Mixed Trace Gases

Because of our incomplete understanding of chemical processes, and their latitudinal and temporal dependence, it is not possible to quantify accurately the indirect GWPs. As noted above, the indirect GWPs reported in IPCC (1990) are likely to be in error and should not be used. In particular, the value for NO_x was probably overestimated by a substantial amount (Johnson *et al.*, 1992). A we are not yet in a position to calculate new i GWPs, we can estimate the sign most likely fo compounds based on current understanding (se A2.1). For example, the indirect GWP for met positive and could be comparable in magnitude direct value. Because the weight of evidence sugge halocarbons are largely responsible for the observe stratospheric ozone loss over the past decade (1992), chlorine- and bromine-containing compou likely to have negative indirect values. Although not itself involved in chemical reactions affect concentrations of radiatively active species, it could affect chemical processes through its influences on the atmospheric thermal structure. Other compounds such as CO, NMHC and NO_x indirectly affect the radiative balance of the atmosphere through changes in tropospheric ozone and OH (see Section A2.5). For such short-lived gases, however, the GWP concept may have little practical applicability.

IPCC 1992 Review:

Conclusions due in part to mistaken belief that impacts of CO and NOx would be likewise short lived.



1994

2

Other Trace Gases and Atmospheric Chemistry

M. PRATHER, R. DERWENT, D. EHHALT, P. FRASER,
E. SANHUEZA, X. ZHOU

Contributors:
F. Alyea, T. Bradshaw, J. Butler, M.A. Carroll, D. Cunnold, E. Dlugokencky, J. Elkins, D. Etheridge, D. Fisher, P. Guthrie, N. Harris, I. Isaksen, D.J. Jacob, C.E. Johnson, J. Kaye, S. Liu, C.T. McElroy, P. Novelli, J. Penner, R. Prinn, W. Reeburgh, J. Richardson, B. Ridley, T. Rudolph, P. Simmonds, L.P. Steele, F. Stordal, R. Weiss, A. Volz-Thomas, A. Wahner, D. Wuebbles

Methane is the only long-lived gas that has clearly identified chemical feedbacks: increases in atmospheric CH_4 reduce the concentration of tropospheric hydroxyl radical (OH), increase the CH_4 lifetime and hence amplify the original CH_4 perturbation. A recent analysis has shown that these feedbacks result in an adjustment time for additional emissions of CH_4 equal to 14.5 ± 2.5 years based on a "budget" lifetime of about 10 years that reflects atmospheric chemical losses alone. It is uncertain how much the adjustment time would be affected by the small biological sink, and a range of 11 to 17 years encompasses this additional uncertainty. This lengthening of the effective duration of a CH_4 pulse applies also to any derived perturbations (e.g., in tropospheric O_3).

2.2.2 Atmospheric Adjustment Times of the Trace Gases

The budget of a trace gas is defined by its sources and sinks. The lifetime describes the rate at which the compound is removed from the atmosphere by chemical processes or by irreversible uptake by the land or ocean. If emissions are uniform, the concentration of a trace gas builds up to a steady-state value at which the product of the global mean abundance (Tg) with the inverse global mean lifetime (1/yr) balances the emissions (Tg/yr). The sum over the chemical rates described above defines the budget of a trace gas (i.e., the sources and sinks) and thus the time-scale for a small perturbation in its abundance to disappear. This time is defined formally as the "adjustment time", and is the essential quantity used in evaluating indices such as the Greenhouse Warming Potential (GWP). For a

However, the concept of an extended adjustment time for perturbations has not been applied to GWPs until this assessment. The ratio of adjustment time to lifetime is greater than one and is independent of the magnitude of the methane perturbation for modest changes (Prather, 1994). Because of differing NO_x and NMHC fields.

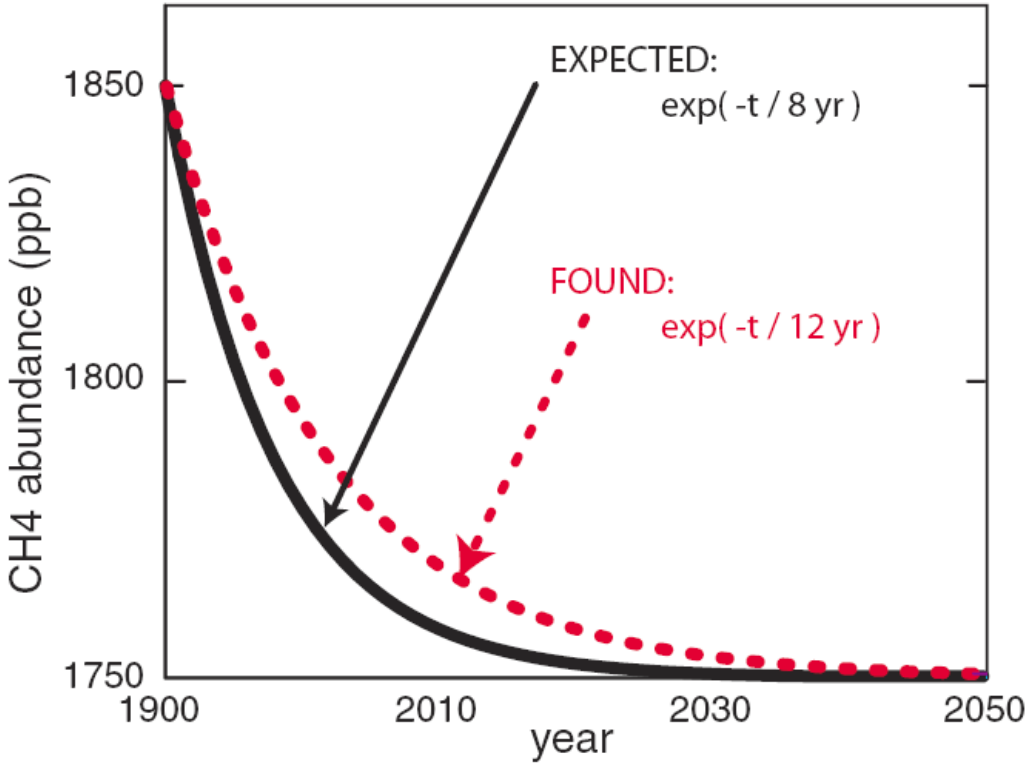
WHY ?

Prather, M.J., 1994: Lifetimes and eigenstates in atmospheric chemistry. *Geophys. Res. Lett.*, **21**, 801-804.

Tropospheric CH_4 – OH chemistry: Delayed recovery of a perturbation

Don Fisher presented a conundrum at the ***1993 AFEAS workshop***:

With a 2-D global atmospheric chemistry model, a pulse of CH_4 did not decay with the expected steady-state lifetime (~8 yr) but with one that was notably longer (~12 yr). The delayed time scale was independent of the magnitude of the perturbation!



GEOPHYSICAL RESEARCH LETTERS, VOL. 21, NO. 9, PAGES 801-804, MAY 1, 1994

Lifetimes and eigenstates in atmospheric chemistry

Michael J. Prather

Earth System Science, University of California at Irvine

Abstract. The time scales and mode of the atmosphere's response to chemical perturbations are defined by the eigenvalues and eigenvectors of the system. The eigenstates of a simplified one-box CH_4-CO-OH system are analyzed. The longest time constant (smallest eigenvalue) always exceeds the lifetime defined by the steady-state loss frequency for CH_4, the longest lived gas. Thus, the extent of a CH_4 perturbation—the methane response time—is always longer than predicted by the steady-state lifetime and is independent of size of the perturbation in the linear limit. This lengthening of the atmospheric recovery time can be diagnosed by how close we are to a chemically unstable troposphere, i.e., how much OH production exceeds that minimum needed to oxidize just the global emissions of CH_4, CO, and other hydrocarbons and species.

The chemical reactions of the CH_4-CO-OH system considered here are

$$OH + CH_4 \Rightarrow \text{(multiple steps)} \Rightarrow CO + \text{products} \quad (1)$$

$$OH + CO \Rightarrow CO_2 + H \quad (2)$$

$$OH + X \Rightarrow \text{products} \quad (3)$$

with rates

$$R_1 = k_1 [OH] [CH_4] \quad (4)$$

$$R_2 = k_2 [OH] [CO] \quad (5)$$

$$R_3 = k_3 [OH] [X]. \quad (6)$$

The only product we are concerned with is the production of CO in R_1. The inclusion of surrogate X allows for OH sinks that are independent of the CH_4-CO system. The time-dependent equations describing the concentrations $[CH_4]$, [CO], and [OH] are then,

$$d[CH_4]/dt = S_{CH4} - R_1 \quad (7)$$

$$d[CO]/dt = S_{CO} + R_1 - R_2 \quad (8)$$

$$d[OH]/dt = S_{OH} - R_1 - R_2 - R_3 \quad (9)$$

Tropospheric CH_4 – OH chemistry: Delayed recovery of a perturbation

Consider a simplified schematic of the global atmospheric CH_4-CO-OH chemical system as three reactions (Prather, 1994, 1996)

$CH_4 + OH \rightarrow ... \rightarrow CO$	$R_5 = k_5 [CH_4] [OH]$	$k_5 = 1.266 \times 10^{-7}\ s^{-1} ppt^{-1}$
$CO + OH \rightarrow ...$	$R_6 = k_6 [CO] [OH]$	$k_6 = 5.08 \times 10^{-6}\ s^{-1} ppt^{-1}$
$OH + X \rightarrow ...$	$R_7 = k_7 [X] [OH]$	$k_7 [X] = 1.062\ s^{-1}$

Given constant sources (S) for these gases the rate equations are

$$d[CH_4]/dt = S_{CH4} - R_5$$
$$d[CO]/dt = S_{CO} + R_5 - R_6$$
$$d[OH]/dt = S_{OH} - R_5 - R_6 - R_7$$

We can pick reasonable source terms to give results that are typical of the globally averaged atmosphere:

$S_{CH4} = 177$ ppb/yr $\quad S_{CO} = 240$ ppb/yr $\quad S_{OH} = 1464$ ppb/yr

$[CH_4] = 1704$ ppb $\quad [CO] = 100$ ppb $\quad [OH] = 0.026$ ppt

Tropospheric CH_4 – OH chemistry: Delayed recovery of a perturbation

The Jacobian (J) of the chemical system is calculated from

$$\begin{pmatrix} \partial(d[CH_4]/dt)/\partial[CH_4] & \partial(d[CH_4]/dt)/\partial[CO] & \partial(d[CH_4]/dt)/\partial[OH] \\ \partial(d[CO]/dt)/\partial[CH_4] & \partial(d[CO]/dt)/\partial[CO] & \partial(d[CO]/dt)/\partial[OH] \\ \partial(d[OH]/dt)/\partial[CH_4] & \partial(d[OH]/dt)/\partial[CO] & \partial(d[OH]/dt)/\partial[OH] \end{pmatrix}$$

and at steady-state has the value (all units are yr^{-1})

- 0.104	0	$- 6.81 \times 10^6$
+0.104	***- 4.17***	$- 9.23 \times 10^6$
- 0.104	- 4.17	$\boldsymbol{- 56.35 \times 10^6}$

The diagonal elements are the negative inverse of the traditionally defined lifetimes:

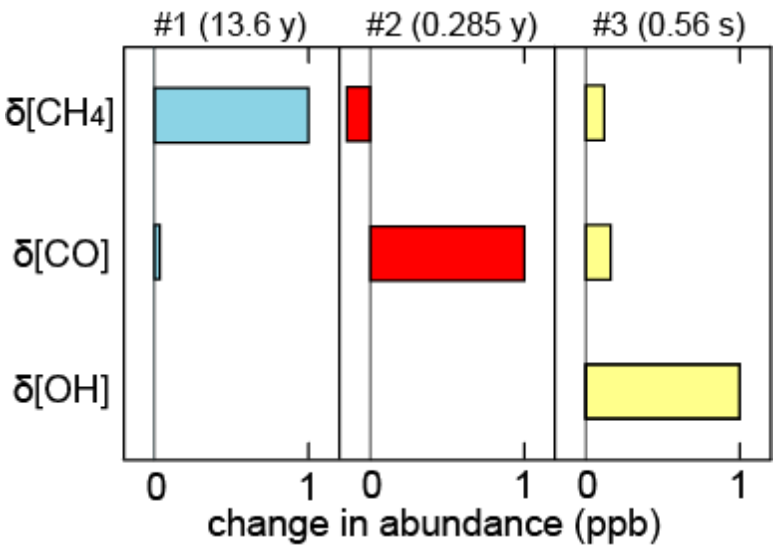
9.6 yr for CH_4

0.240 yr for CO

0.56 s for OH

Tropospheric CH_4 – OH chemistry: Delayed recovery of a perturbation

The inverse-negative eigenvalues ($T_i = -1/\lambda_i$) and eigenvectors are:



Thus an instantaneous perturbation of $\delta[CH_4] = 1$ becomes a perturbation to all three species and over all three time scales:

$$\delta[CH_4](t) = +0.995\, e^{-t/13.6} + 0.005\, e^{-t/0.285} + 0.000\, e^{-t/0.000000018}$$
$$\delta[CO](t) = +0.035\, e^{-t/13.6} - 0.035\, e^{-t/0.285} + 0.000 \ldots$$
$$\delta[OH](t) = \ldots$$

Tropospheric CH_4 – OH chemistry: Delayed recovery of a perturbation

More surprisingly, a perturbation to CO alone, **δ[CO]=1,** causes a significant perturbation to CH_4 that is "unmasked" in a few months:

$$\delta[CO](t) \approx +0.005\, e^{-t/13.6} + 0.995\, e^{-t/0.285}$$

$$\delta[CH_4](t) \approx +0.15\, e^{-t/13.6} - 0.15\, e^{-t/0.285}$$

The off-diagonal elements in the Jacobian cause a coupling across all species, <u>including</u> excitation of the 13.6-yr CH_4-like chemical mode in response to a perturbation of CO alone.

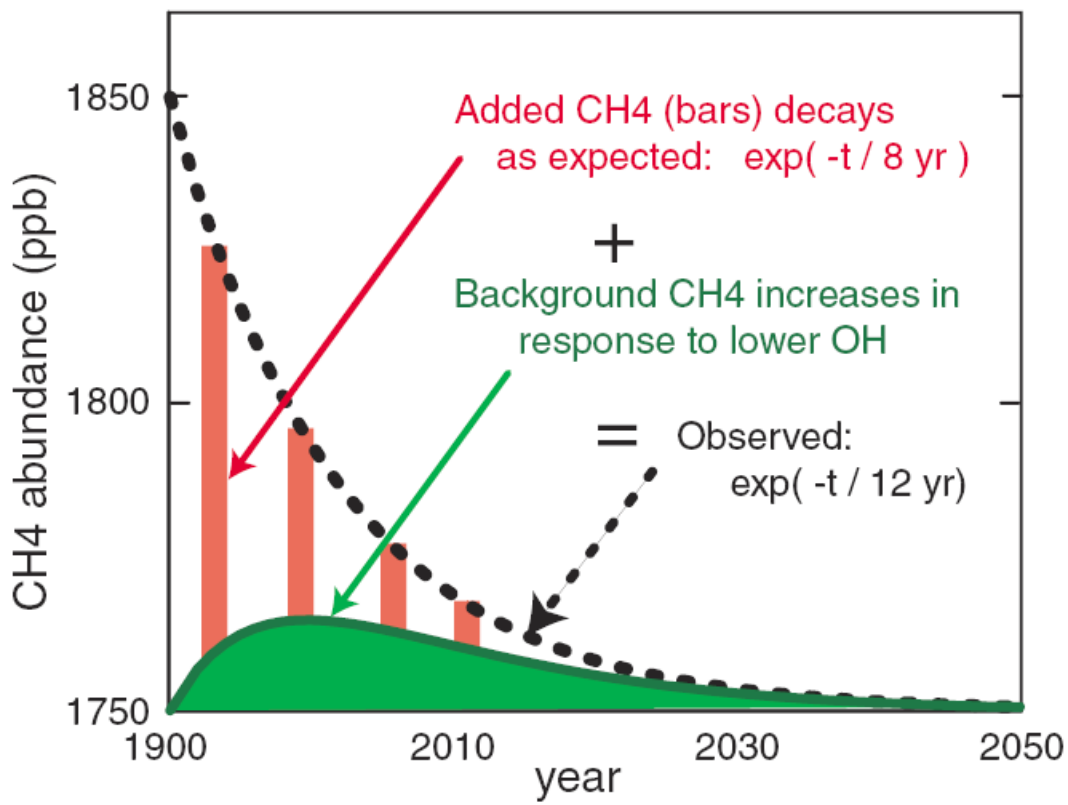
Tropospheric CH_4 – OH chemistry: Delayed recovery of a perturbation

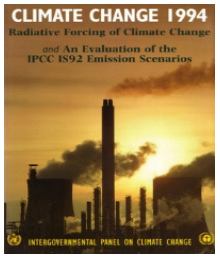
We now can understand Fisher's results as a coupled system:

if colored separately, the added CH_4 decays with an 8-yr e-fold,

background CH_4 is perturbed in proportion to the added CH_4,

and the total perturbation decays with a 12-yr e-fold.





1994

2

Other Trace Gases and Atmospheric Chemistry

Multi-model assessment of CH_4 feedback factor first derived from Prather 1994 box model.

M. PRATHER, R. DERWENT, D. EHHALT, P. FRASER,
E. SANHUEZA, X. ZHOU

Contributors:
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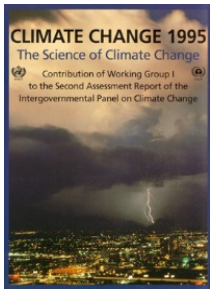
W. Reeburgh, J. Richardson, B. Ridley, T. Rudolph, P. Simmonds, L.P.
F. Stordal, R. Weiss, A. Volz-Thomas, A. Wahner, D. Wuebbles

***Table 2.9:** Inferred CH_4 response time from the CH_4 perturbation simulations.*

Model code	Feedback factor	Adjustment time/lifetime
B	-0.20%	1.29
M	-0.17%	1.23†
O	-0.35%	1.62
P	-0.22%	1.32
R	-0.26%	1.39
(R)	-0.18%	1.26†
T	-0.34%	1.61

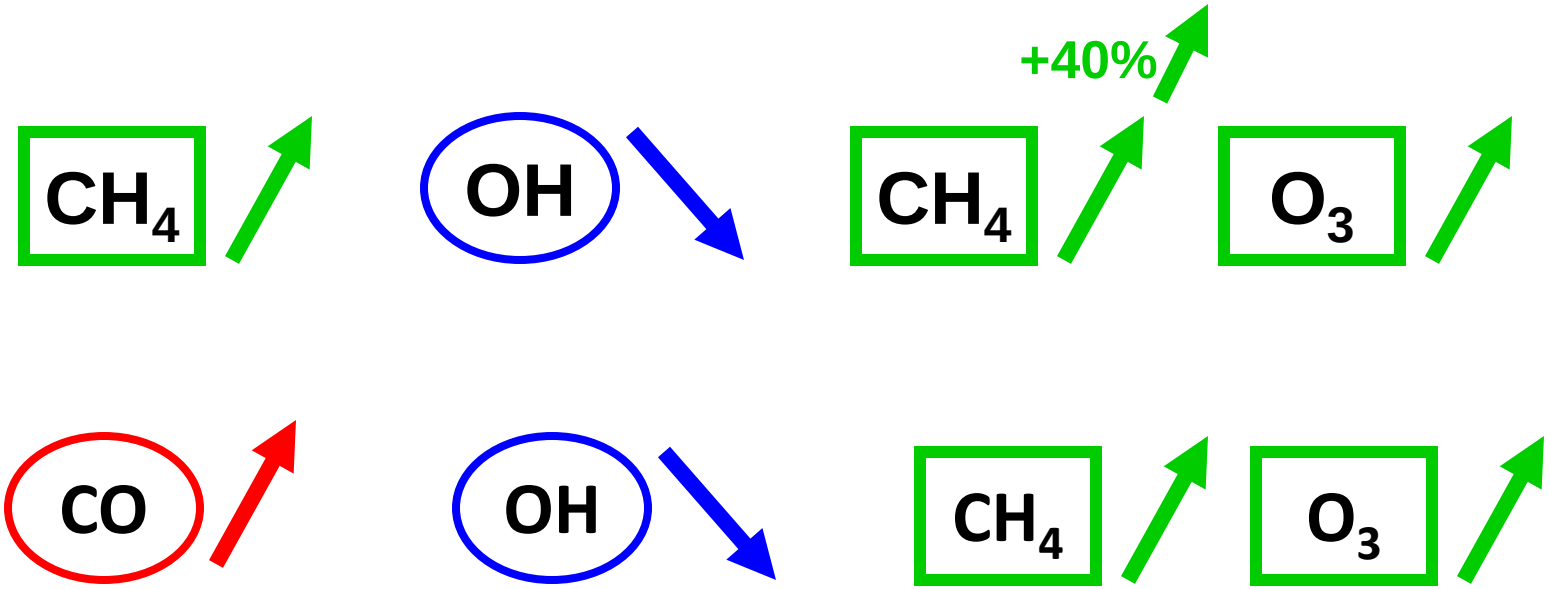
Note: Feedback factor = relative change (%) in the globally averaged CH_4 loss frequency (i.e., [OH]) for a +1% increase in CH_4 concentrations.
† These models use fixed CO concentrations and so underestimate this ratio.



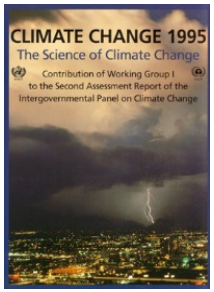
1995

CH_4 climate forcing from

1) feedback on its own lifetime
2) increase in tropospheric O_3



Isaksen & Hov, 1987
Prather, 1994
IPCC SAR (multi-model assessment), 1995/1996



1995

2

lifetimes from OH
lifetimes with feedbacks

Radiative Forcing of Climate Change

D. SCHIMEL, D. ALVES, I. ENTI
F. JOOS, D. RAYNAUD, T. WIGL
M. PRATHER, R. DERWENT, D. I
E. SANHUEZA, X. ZHOU (2.2)
P. JONAS, R. CHARLSON, H. RO
K.P. SHINE, Y. FOUQUART, V. R
S. SOLOMON, J. SRINIVASAN (2
D. ALBRITTON, R. DERWENT, I.

Table 2.2: *Lifetimes for radiatively active gases and halocarbons*

SPECIES		LIFETIME		CONCENTRATION (ppbv)		CURRENT GROWTH	RADIATIVE FORCING	
		Year	Uncert.	1992	pre-ind.	ppbv/yr	Wm^{-2} /ppbv	Wm^{-2}
NATURAL AND ANTHROPOGENICALLY INFLUENCED GASES								
carbon dioxide	CO_2	variable		356,000	278,000	1,600	1.8×10^{-5}	1.56
methane	CH_4@	12.2	25%	1714	700	8	3.7×10^{-4}	0.47
nitrous oxide	N_2O	120		311	275	0.8	3.7×10^{-3}	0.14
methyl chloride	CH_3Cl	1.5	25%	~0.6	~0.6	~0		0
methyl bromide	CH_3Br	1.2	32%	0.010	< 0.010	~0		0
chloroform	$CHCl_3$	0.51	300%	~0.012		~0	0.017	
methylene chloride	CH_2Cl_2	0.46	200%	~0.030		~0	0.03	
carbon monoxide	CO	0.25		50-150		~0		$
GASES PHASED OUT BEFORE 2000 UNDER THE MONTREAL PROTOCOL AND ITS AMENDMENTS								
CFC-11	CCl_3F	50	10%	0.268	0	+0.000**	0.22	0.06
CFC-12	CCl_2F_2	102		0.503	0	+0.007**	0.28	0.14
CFC-113	CCl_2FCClF_2	85		0.082	0	0.000**	0.28	0.02
CFC-114	$CClF_2CClF_2$	300		0.020	0		0.32	0.007
CFC-115	CF_3CClF_2	1700		< 0.01	0		0.26	<0.003
carbon tetrachloride	CCl_4	42		0.132	0	~0.0005**	0.10	0.01
methyl chloroform	CH_3CCl_3	4.9	8%	0.135#	0	~0.010**	0.05	0.007
halon-1211	$CBrClF_2$	20		0.007	0	.00015		
halon-1301	$CBrF_3$	65		0.003	0	.0002	0.28	
halon-2402	$CBrF_2CBrF_2$	20		0.0007	0			
CHLORINATED HYDROCARBONS CONTROLLED BY THE MONTREAL PROTOCOL AND ITS AMENDMENTS								
HCFC-22	$CHClF_2$	12.1	20%	0.100	0	+0.005**	0.19	0.02
HCFC-123	CF_3CHCl_2	1.4	25%		0		0.18	

SCIENCE • VOL. 279 • 27 FEBRUARY 1998

Time Scales in Atmospheric Chemistry: Coupled Perturbations to N_2O, NO_y, and O_3

Michael J. Prather

Opposite to that of CH_4, the N_2O-NOy-O_3 coupling actually reduces the residence time of an N_2O perturbation.

Nitrous oxide (N_2O) 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 N_2O and stratospheric ozone (O_3), which can easily be decomposed into its natural modes. The primary, longest lived mode describes most of the atmospheric perturbation due to anthropogenic N_2O sources, and this pattern may be observable. The photolytic link between O_3 and N_2O is identified as the mechanism causing this mode to decay 10 to 15 percent more rapidly than the N_2O mean atmospheric lifetime, affecting the inference of anthropogenic sources.

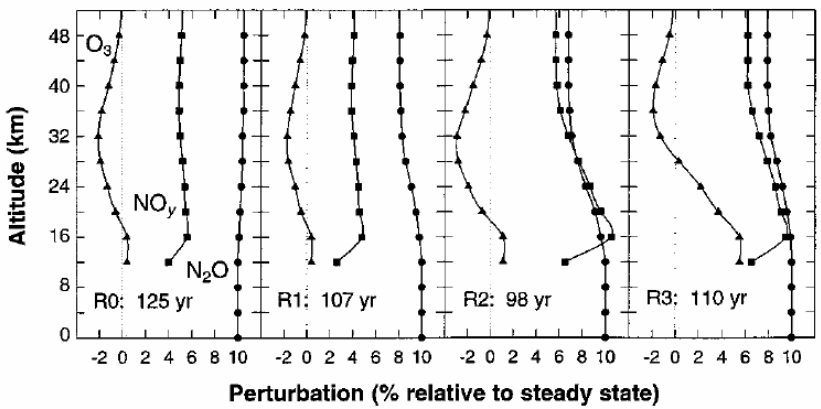
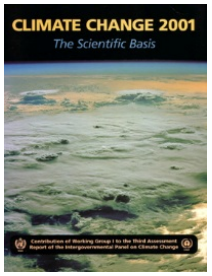


Fig. 3. The primary (longest lived) natural mode of the coupled {N_2O, NO_y, O_3}-system expressed as a perturbation (percent change) to the steady-state concentrations of N_2O (circles), NO_y (squares), and O_3 (triangles). The mode is scaled to give a +10% change in N_2O at the surface. The mean steady-state 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).

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.



2001

4

Atmospheric Chemistry and Greenhouse Gases

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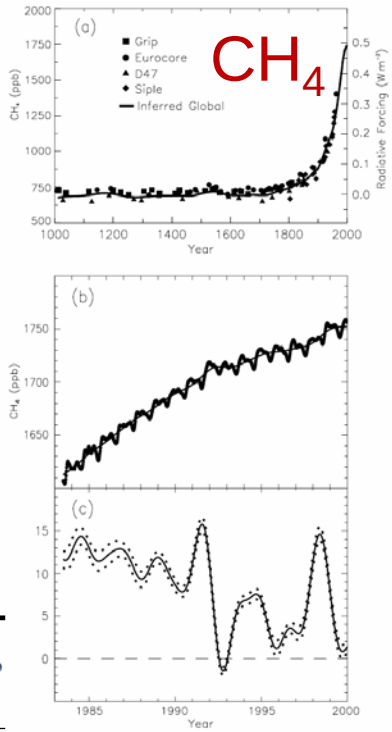

ure 4.1: (a) Change in CH_4 abundance (mole fraction, in ppb = 10^{-9})

Table 4.1(a): Chemically reactive greenhouse gases and their precursors: abundances, trends, budgets, lifetimes, and GWPs.

Chemical species	Formula	Abundance[a] ppt 1998	Abundance[a] ppt 1750	Trend ppt/yr[a] 1990s	Annual emission late 90s	Life-time (yr)	100-yr GWP[b]
Methane	CH_4(ppb)	1745	700	7.0	600 Tg	8.4/12[c]	23
Nitrous oxide	N_2O (ppb)	314	270	0.8	16.4 TgN	120/114[c]	296
Perfluoromethane	CF_4	80	40	1.0	~15 Gg	>50000	5700
Perfluoroethane	C_2F_6	3.0	0	0.08	~2 Gg	10000	11900
Sulphur hexafluoride	SF_6	4.2	0	0.24	~6 Gg	3200	22100
HFC-23	CHF_3	14	0	0.55	~7 Gg	260	12000
HFC-134a	CF_3CH_2F	7.5	0	2.0	~25 Gg	13.8	1300
HFC-152a	CH_3CHF_2	0.5	0	0.1	~4 Gg	1.40	120

Lifetimes revised again

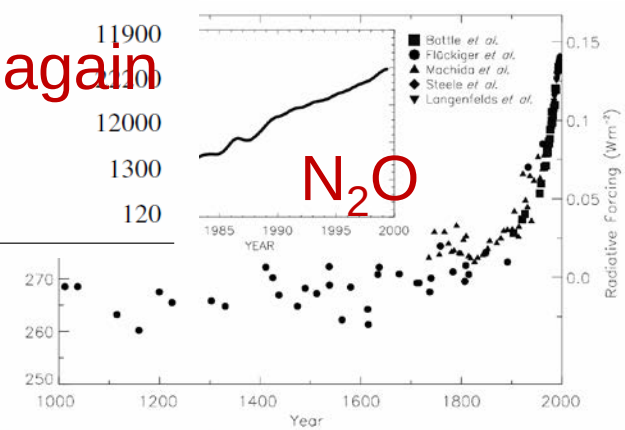

Figure 4.2: Change in N_2O abundance for the last 1,000 years as determined from ice cores, firn, and whole air samples. Data sets are from: Machida *et al.* (1995); Battle *et al.* (1996); Langenfelds *et al.* (1996); Steele *et al.* (1996); Flückiger *et al.* (1999). Radiative forcing, approximated by a linear scale, is plotted on the right axis. Deseasonalised global averages are plotted in the inset (Butler *et al.*, 1998b).

GEOPHYSICAL RESEARCH LETTERS, VOL. 28, NO. 9, PAGES 1719-1722, MAY 1, 2001

Indirect long-term global radiative cooling from NO_x emissions

Discovery – linkages across time scales and species

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Michael J. Prather

Earth System Science, Univ

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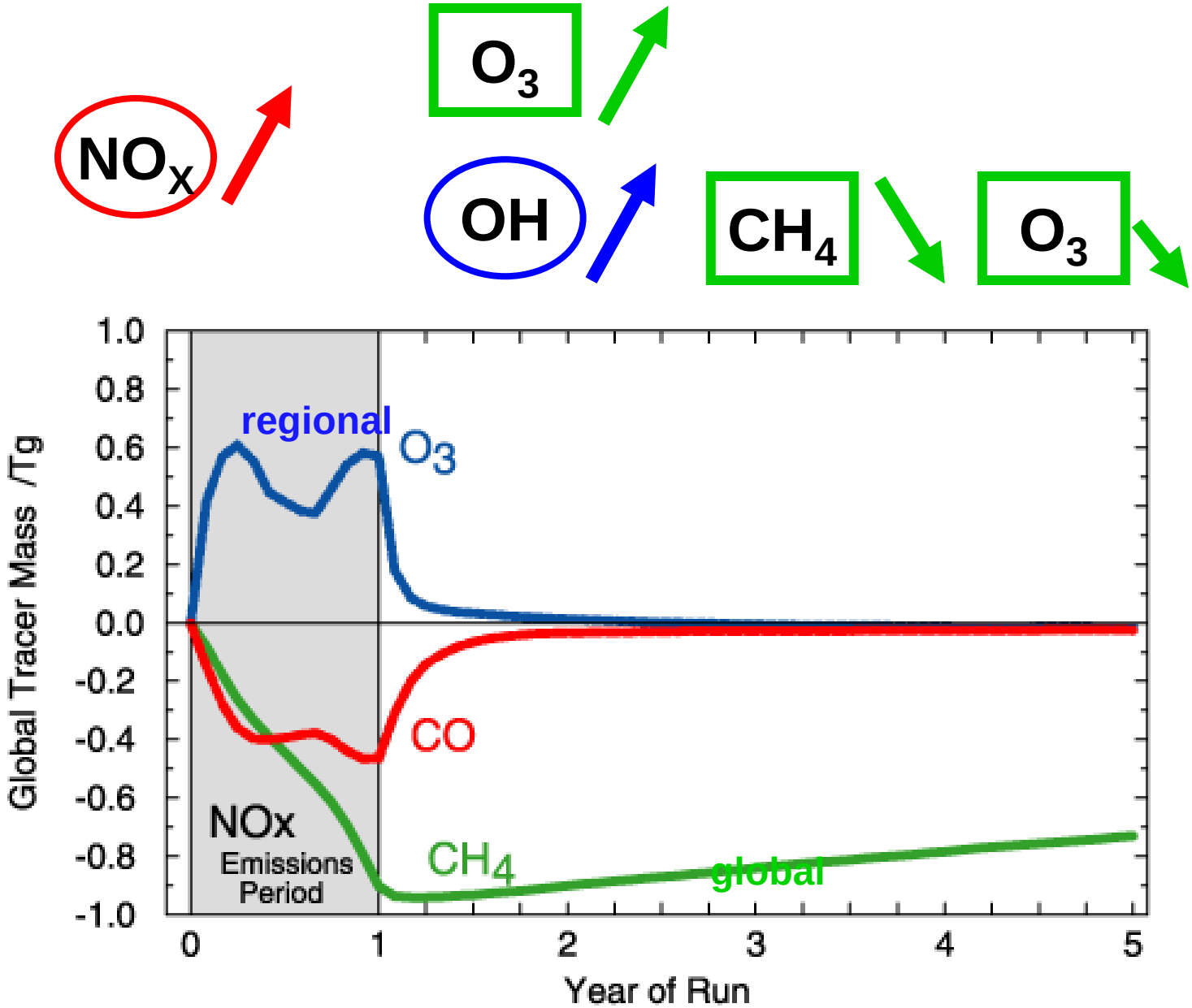
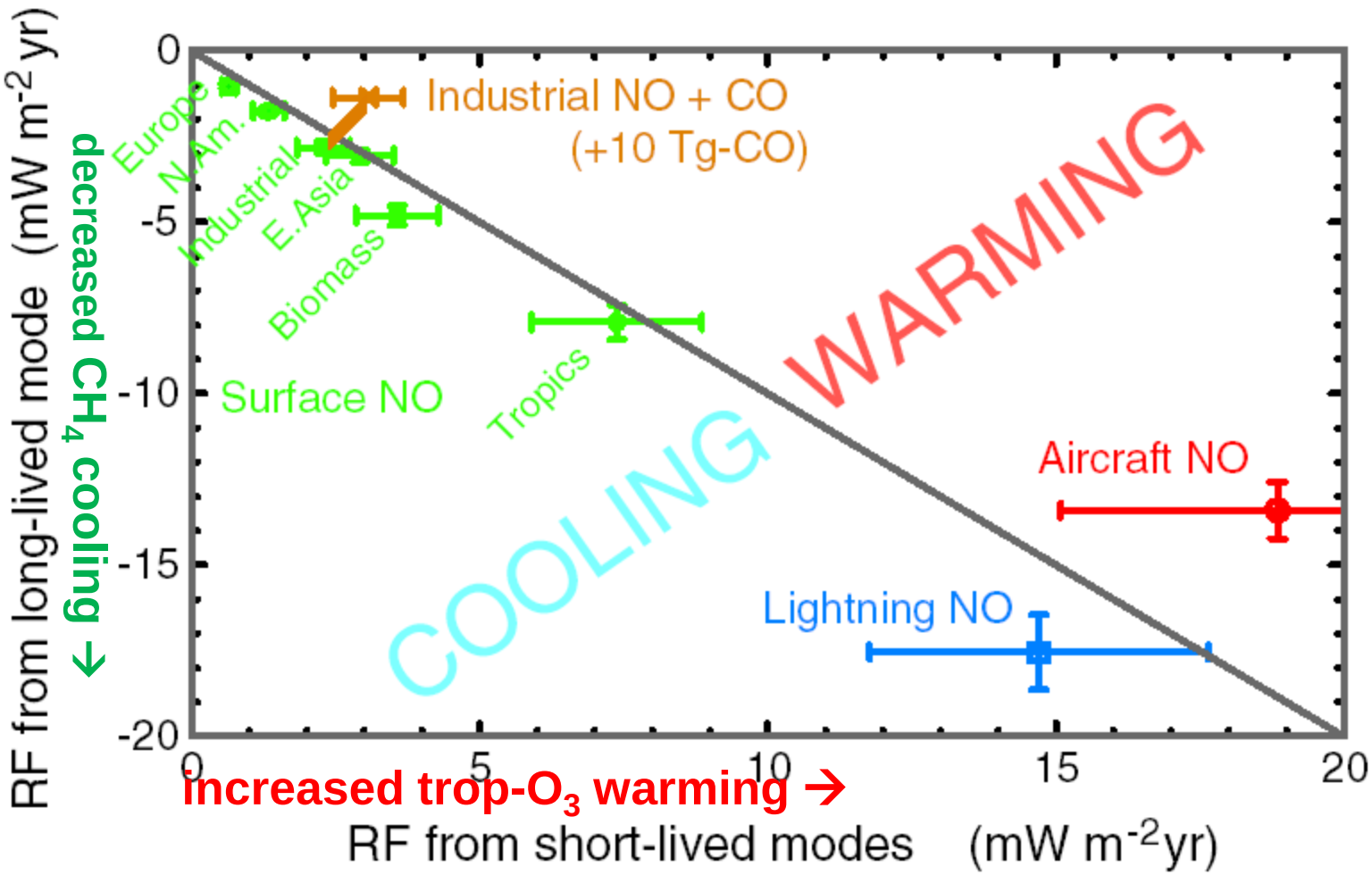
Abstract. Anthropogenic emissions of short-lived, chemically reactive gases, such as NO_x and CO, are known to influence climate by altering the chemistry of the global troposphere and thereby the abundance of the greenhouse gases O_3, CH_4 and the HFCs. This study uses the characteristics of the natural modes of the tropospheric chemical system to decompose the greenhouse effect of NO_x and CO emissions into (i) short-lived modes involving predominantly tropospheric O_3 and (ii) the long-lived mode involving a global coupled CH_4-CO-O_3 perturbation. Combining these two classes of greenhouse perturbations—large, short-lived, regional O_3 increases and smaller, long-lived, global decreases in CH_4 and O_3—we find that most types of anthropogenic NO_x emissions lead to a negative radiative forcing and an overall cooling of the earth.

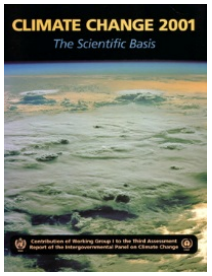


0.5 Tg-N of NOx *(Wild, Prather, Akimoto, 2001)*

Not all NOx is created equal: most NOx falls along the "climate-neutral" line, but NOx emissions in tropics or at high-alt » EU at surface.



0.5 Tg-N of NOx *(Wild, Prather, Akimoto, 2001)*



2001

4

Atmospheric Chemistry and Greenhouse Gases

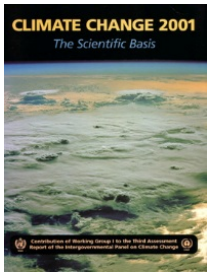
Co-ordinating Lead Authors
M. Prather, D. Ehhalt

Table 4.3: Methane lifetime and feedback on tropospheric OH[a] for the 1990s.

CTM	lifetime vs. OH(yr)[b]	δln(OH)/ δln(CH_4)	s= δln(LT)/ δln(CH_4)	PT/LT
IASB	8.1	–0.31	+0.27	1.37
KNMI	9.8	–0.35	+0.31	1.45
MPIC	8.5	–0.29	+0.25	1.33
UCI	9.0	–0.34 (–0.38)[c]	+0.30	1.43
UIO1	6.5	–0.33	+0.29	1.41
UKMO	8.3	–0.31 (–0.34)[c]	+0.27	1.37
ULAQ	13.8	–0.29	+0.25	1.33
TAR value[d]	9.6	–0.32		1.4

Table 4.5: Nitrous oxide lifetime feedback and residence time.

Models	Contributor	Lifetime LT (yr)	Sensitivity, s=∂ln(LT)/ ∂ln(B)	Decay Time of mode (yr)
AER 2D	Ko and Weisenstein	111	–0.062	102
GSFC 2D	Jackman	137	–0.052	127
UCI 1D	Prather	119	–0.046	110
Oslo 2D	Rognerud	97	–0.061	

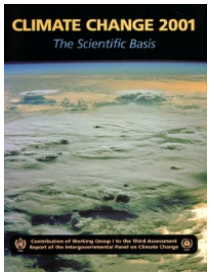


2001

CH_4 self-feedback, TAR

Changes in atmospheric composition and chemistry over the past century have affected, and those projected into the future will affect, the lifetimes of many greenhouse gases and thus alter the climate forcing of anthropogenic emissions:

The atmospheric lifetime relates emissions of a component to its atmospheric burden. In some cases, for instance for methane, a change in emissions perturbs the chemistry and thus the corresponding lifetime. The CH_4 feedback effect amplifies the climate forcing of an addition of CH_4 to the current atmosphere by lengthening the perturbation lifetime relative to the global atmospheric lifetime of CH_4 by a factor of 1.4. This earlier finding is corroborated here by new model studies that also predict only small changes in this CH_4 feedback for the different scenarios projected to year 2100. Another feedback has been identified for the addition of N_2O to the atmosphere; it is associated with stratospheric O_3 chemistry and shortens the perturbation lifetime relative to the global atmospheric lifetime of N_2O by about 5%.



2001

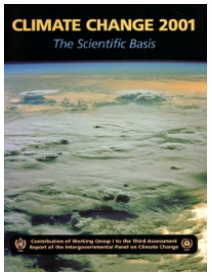
Executive Summary

CO indirect RF

Two important new findings since the IPCC WGI Second Assessment Report (IPCC, 1996) (hereafter SAR) demonstrate the importance of atmospheric chemistry in controlling greenhouse gases:

Currently, tropospheric ozone (O_3) is the third most important greenhouse gas after carbon dioxide (CO_2) and methane (CH_4). It is a product of photochemistry, and its future abundance is controlled primarily by emissions of CH_4, carbon monoxide (CO), nitrogen oxides (NO_x), and volatile organic compounds (VOC). There is now greater confidence in the model assessment of the increase in tropospheric O_3 since the pre-industrial period, which amounts to 30% when globally averaged, as well as the response to future emissions. For scenarios in which the CH_4 abundance doubles and anthropogenic CO and NO_x emissions triple, the tropospheric O_3 abundance is predicted to increase by an additional 50% above today's abundance.

CO is identified as an important indirect greenhouse gas. An addition of CO to the atmosphere perturbs the OH-CH_4-O_3 chemistry. Model calculations indicate that the emission of 100 Mt of CO stimulates an atmospheric chemistry perturbation that is equivalent to direct emission of about 5 Mt of CH_4.



2001

4

Atmospheric Chemistry and Greenhouse Gases

First trop. O_3 trend time series in real units! (not %).
Iconic times series (Logan, 1999) – not CO_2!

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P. Midgley, M. Wang

Contributing Authors

Table 4.12: Tropospheric ozone budgets for circa 1990 conditions from a sample of globa

CTM	STE	Prod	Loss (Tg/yr)	P–L	SURF	Burden (Tg)
MATCH	1440	2490	3300	−810	620	
MATCH-MPIC	1103	2334	2812	−478	621	
ECHAM/TM3	768	3979	4065	−86	681	311
ECHAM/TM3 [a]	740	2894	3149	−255	533	266
HARVARD	400	4100	3680	+420	820	310
GCTM	696			+128	825	298
UIO	846			+295	1178	370
ECHAM4	459	3425	3350	+75	534	271
MOZART [b]	391	3018	2511	+507	898	193
STOCHEM	432	4320	3890	+430	862	316
KNMI	1429	2864	3719	−855	574	
UCI	473	4229	3884	+345	812	288

Atmospheric Chemistry and Greenhouse Gases

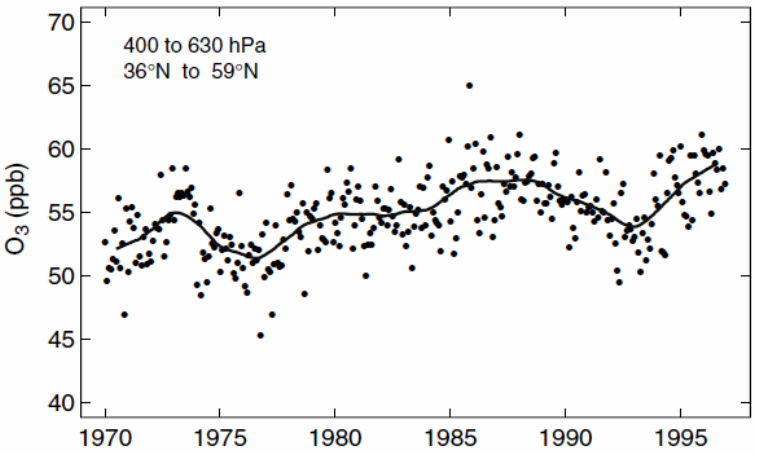


Figure 4.8: Mid-tropospheric O_3 abundance (ppb) in northern mid-latitudes (36°N-59°N) for the years 1970 to 1996. Observations between 630 and 400 hPa are averaged from nine ozone sonde stations (four in North America, three in Europe, two in Japan), following the data analysis of Logan *et al.* (1999). Values are derived from the residuals of the trend fit with the trend added back to allow for discontinuities in the instruments. Monthly data (points) are shown with a smoothed 12-month-running mean (line).

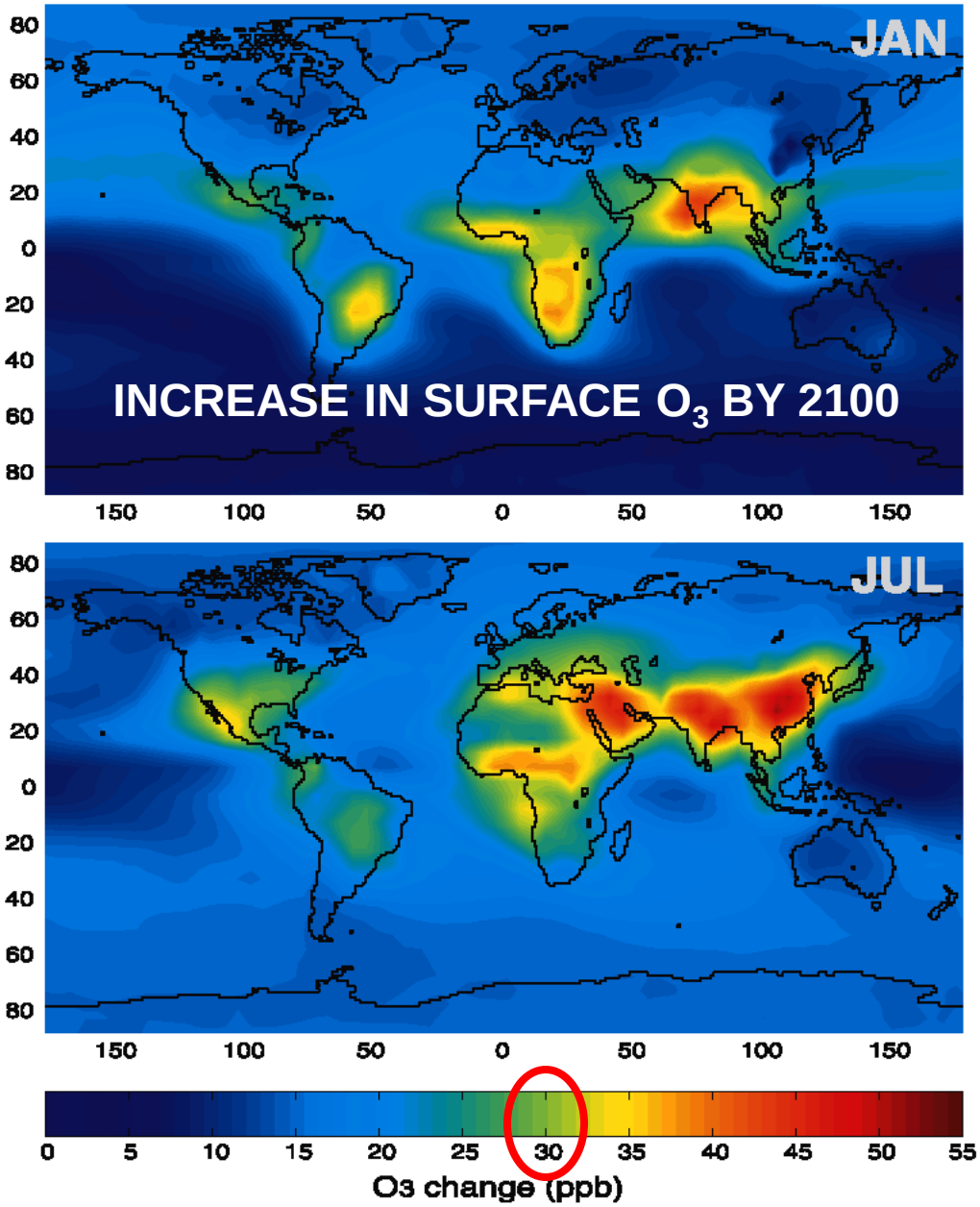
GEOPHYSICAL RESEARCH LETTERS, VOL. 30, NO. 2, 1100, doi:10.1029/2002GL016285, 2003

Fresh air in the 21st century?

Michael Prather,[1] Michael Gauss,[2] Terje Berntsen,[2] Ivar Isaksen,[2] Jostein Sundet,[2] Isabelle Bey,[3] Guy Brasseur,[4] Frank Dentener,[5] Richard Derwent,[6] David Stevenso Lee Grenfell,[7] Didier Hauglustaine,[8] Larry Horowitz,[9] Daniel Jacob,[10] Loretta Mick Mark Lawrence,[11] Rolf von Kuhlmann,[11] Jean-Francois Muller,[12] Giovanni Pitari, Helen Rogers,[14] Matthew Johnson,[14] John Pyle,[14] Kathy Law,[14] Michiel van Weel and Oliver Wild[16]

2003 GRL

IPCC (2001). "Changes projected in the SRES A2 and A1FI scenarios would degrade air quality over much of the globe by increasing background levels of O_3. In northern mid-latitudes during summer, the zonal average increases near the surface are about 30 ppb or more, raising background levels to nearly 80 ppb, threatening attainment of air quality standards over most metropolitan and even rural regions, and compromising crop and forest productivity. This problem reaches across continental boundaries since emissions of NOx influence photochemistry on a hemispheric scale."



PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

Phil. Trans. R. Soc. A (2007) **365**, 1705–1726
doi:10.1098/rsta.2007.2040
Published online 18 May 2007

review of work 1994-2006

Lifetimes and time scales in atmospheric chemistry

By Michael J. Prather*

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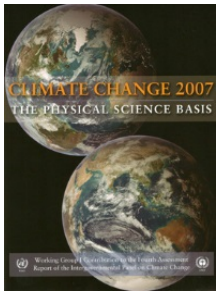
Atmospheric composition is controlled by the emission, photochemistry and transport of many trace gases. Understanding the time scale as well as the chemical and spatial patterns of perturbations to trace gases is needed to evaluate possible environmental damage (e.g. stratospheric ozone depletion or climate change) caused by anthropogenic emissions. This paper reviews lessons learned from treating global atmospheric chemistry as a linearized system and analysing it in terms of eigenvalues.

The results give insight into how emissions of one trace species cause perturbations to another and how transport and chemistry can alter the time scale of the overall perturbation. Further, the eigenvectors describe the fundamental chemical modes, or patterns, of the atmosphere's chemical response to perturbations.

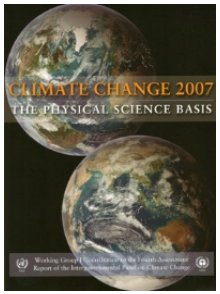


2007

CO indirect GWP

2.10.3.2 Carbon Monoxide

The indirect effects of CO occur through reduced OH levels (leading to enhanced concentrations of CH_4) and enhancement of ozone. The TAR gave a range of 1.0 to 3.0 for the 100-year GWP. Since the TAR, Collins et al. (2002) and Berntsen et al. (2005) have calculated GWPs for CO emissions that range between 1.6 and 2.0, depending on the location of the emissions. Berntsen et al. (2005) found that emissions of CO from Asia had a 25% higher GWP compared to European emissions. Averaging over the TAR values and the new estimates give a mean of 1.9 for the 100-year GWP for CO.



2007

VOC & NOx indirect GWPs

Organic Compound/Study	GWP^{CH_4}	GWP^{O_3}	GWP
Ethane (C_2H_6)	2.9	2.6	5.5
Propane (C_3H_8)	2.7	0.6	3.3
Butane (C_4H_{10})	2.3	1.7	4.0
Ethylene (C_2H_4)	1.5	2.2	3.7
Propylene (C_3H_6)	–2.0	3.8	1.8
Toluene (C_7H_8)	0.2	2.5	2.7
Isoprene (C_5H_8)	1.1	1.6	2.7
Methanol (CH_3OH)	1.6	1.2	2.8
Acetaldehyde (CH_3CHO)	–0.4	1.7	1.3
Acetone (CH_3COCH_3)	0.3	0.2	0.5
Derwent et al. NH surface NO_x[a,b]	–24	11	–12
Derwent et al. SH surface NO_x[a,b]	–64	33	–31
Wild et al., industrial NO_x	–44	32	–12
Berntsen et al., surface NO_x Asia	–31 to –42[c]	55 to 70[c]	25 to 29[c]
Berntsen et al., surface NO_x Europe	–8.6 to –11[c]	8.1 to 12.7	–2.7 to +4.1[c]
Derwent et al., Aircraft NO_x[a,b]	–145	246	100
Wild et al., Aircraft NO_x	–210	340	130
Stevenson et al. Aircraft NO_x	–159	155	3

GEOPHYSICAL RESEARCH LETTERS, VOL. 37, L07805, doi:10.1029/2009GL042243, 2010

Finally finish strat-trop eigenmodes in 3D CTM!

Global long-lived chemical modes excited in a 3-D chemistry transport model: Stratospheric N_2O, NO_y, O_3 and CH_4 chemistry

Juno Hsu[1] and Michael J. Prather[1]

Received 23 December 2009; revised 10 February 2010; accepted 23 February 2010; published 2 April 2010.

REPORTS

Coupling of Nitrous Oxide and Methane by Global Atmospheric Chemistry

Michael J. Prather and Juno Hsu

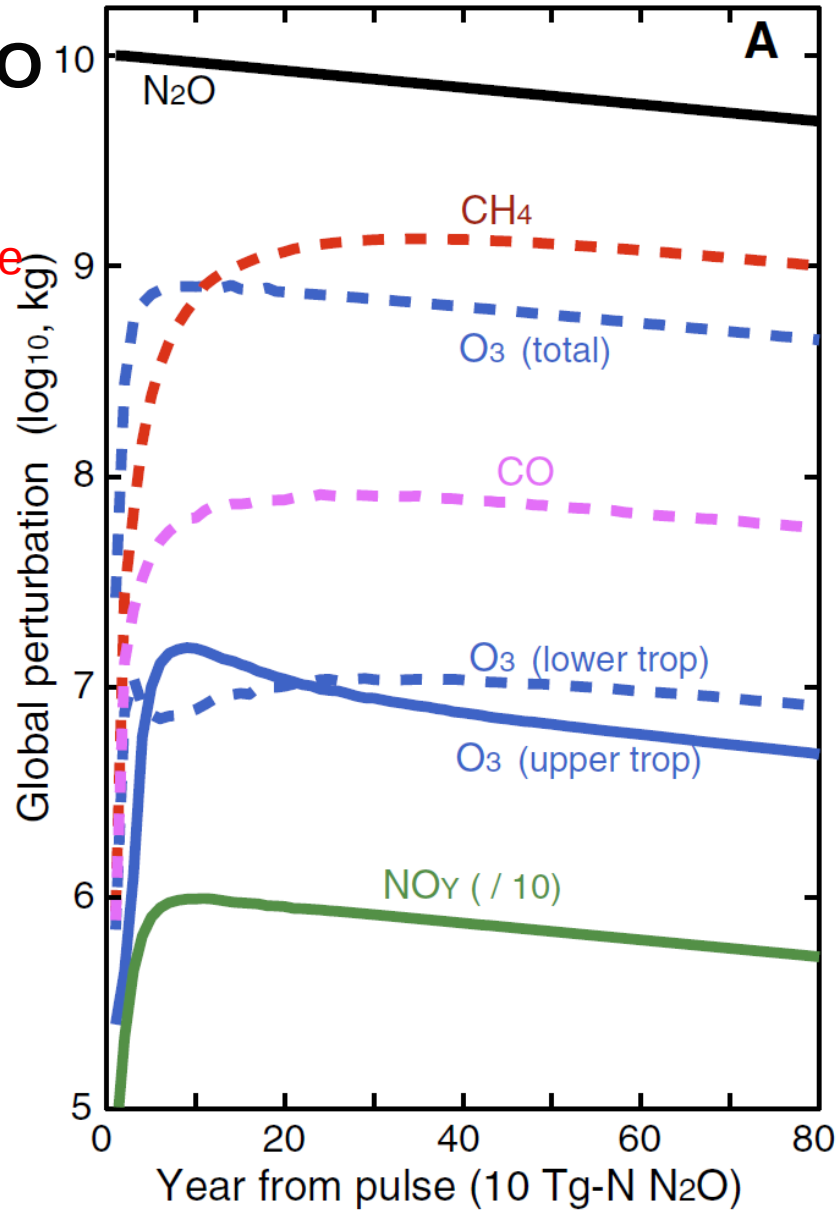
12 NOVEMBER 2010 VOL 330 SCIENCE

Nitrous oxide (N_2O) 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_2O and CH_4 emissions through the coupled chemistries of the stratosphere and troposphere. Specifically, we simulated the coupled perturbations of increased N_2O 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_2O change, –36% by mole fraction, offsets a fraction of the greenhouse effect attributable to N_2O emissions. These CH_4 decreases are tied to the 108-year chemical mode of N_2O, which is nine times longer than the residence time of direct CH_4 emissions.

mode #1 (108 yr) impacts on CH_4, CO, O_3, …

+10 Tg-N N_2O

dashed = negative perturbation



A relatively large reduction in CH_4 (-3.6 ppb) is tied to N_2O increases (+10 ppb)

These all decay with a 108-yr time scale.

N_2O's climate impact is reduced:

(i) **-8.4%** because decay of pulse is faster than the e-fold of the lifetime

(ii) **-4.5%** because of the reduced CH_4.

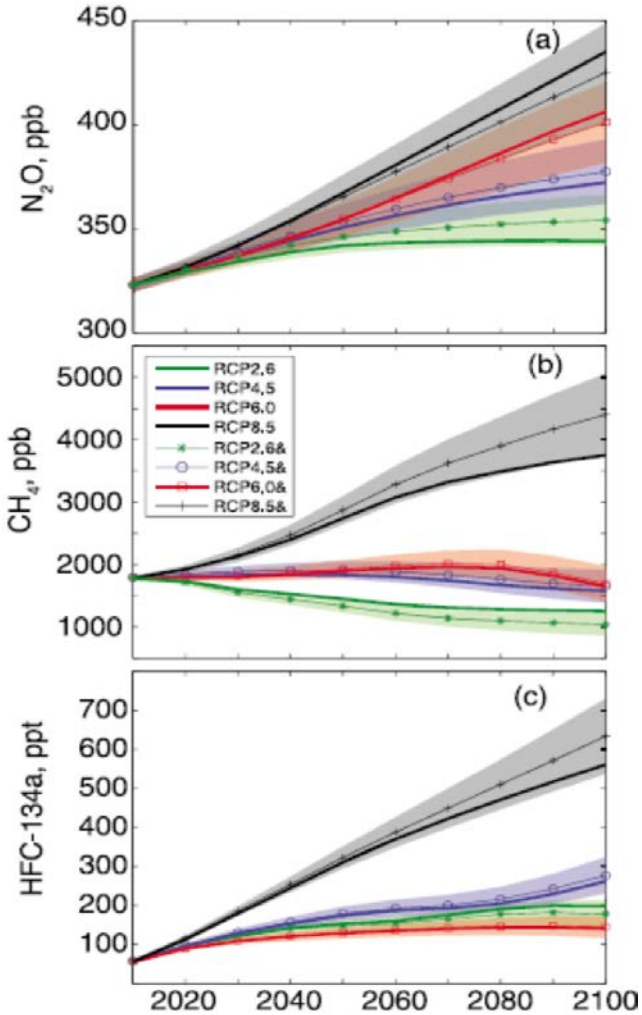
Atmospheric chemistry needed to propagate uncertainty into IPCC

GEOPHYSICAL RESEARCH LETTERS, VOL. 39, L09803, doi:10.1029/2012GL051440, 2012

Reactive greenhouse gas scenarios: Systematic exploration of uncertainties and the role of atmospheric chemistry

Michael J. Prather,[1] Christopher D. Holmes,[1] and Juno Hsu[1]

[1] Knowledge of the atmospheric chemistry of reactive greenhouse gases is needed to accurately quantify the relationship between human activities and climate, and to incorporate uncertainty in our projections of greenhouse gas abundances. We present a method for estimating the fraction of greenhouse gases attributable to human activities, both currently and for future scenarios. Key variables used to calculate the atmospheric chemistry and budgets of major non-CO_2 greenhouse gases are codified along with their uncertainties, and then used to project budgets and abundances under the new climate-change scenarios. This new approach uses our knowledge of changing abundances and lifetimes to estimate current total anthropogenic emissions, independently and possibly more accurately than inventory-based scenarios. We derive a present-day atmospheric lifetime for methane (CH_4) of 9.1 ± 0.9 y and anthropogenic emissions of 352 ± 45 Tg/y (64% of total emissions). For N_2O, corresponding values are 131 ± 10 y and 6.5 ± 1.3 TgN/y (41% of total); and for HFC-134a, the lifetime is 14.2 ± 1.5 y. **Citation:** Prather, M. J., C. D. Holmes, and J. Hsu (2012), Reactive greenhouse gas scenarios: Systematic exploration of uncertainties and the role of atmospheric chemistry, *Geophys. Res. Lett.*, *39*, L09803, doi:10.1029/2012GL051440.



2013

Where's chemistry in the 2013 AR5?

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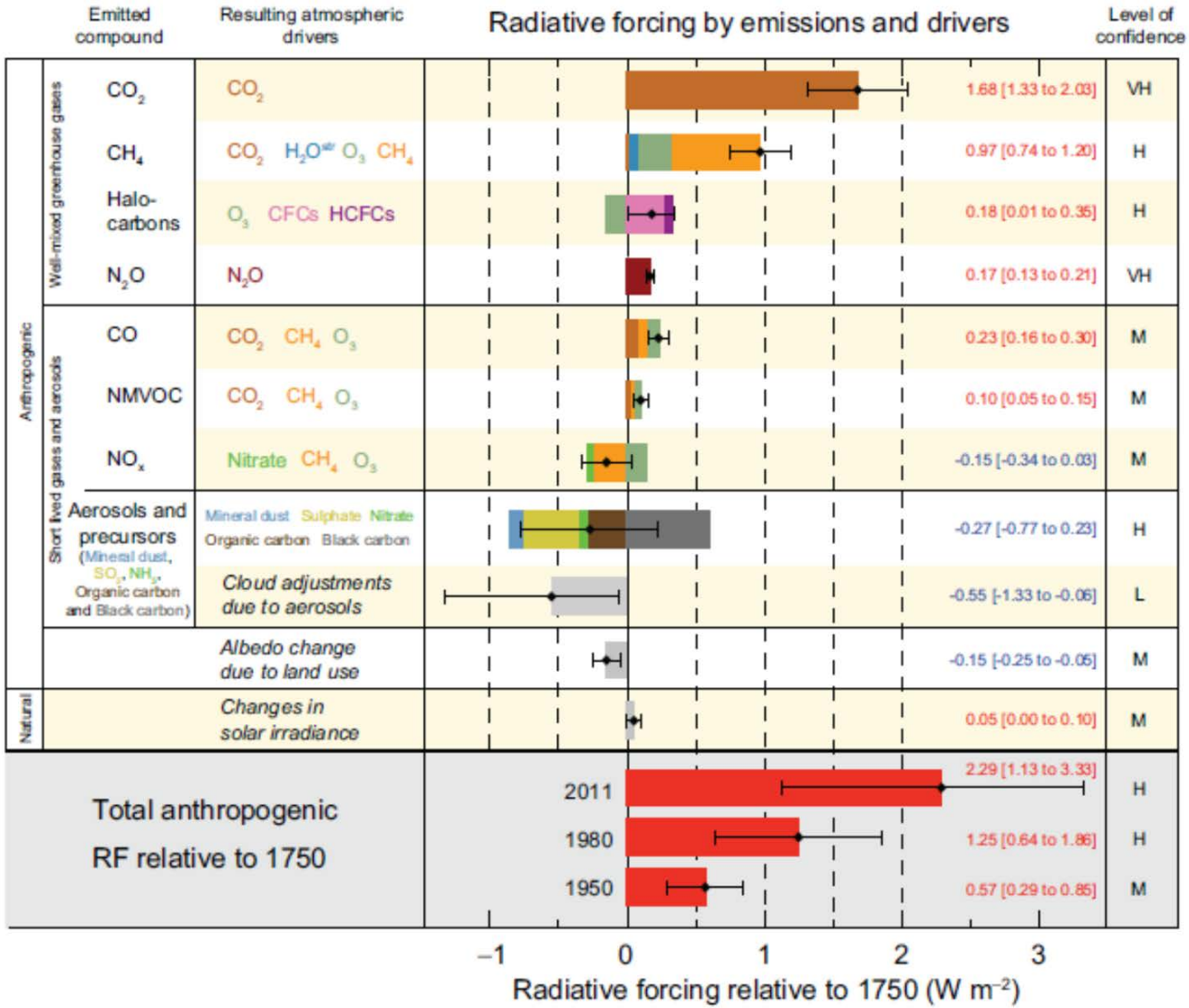
now with Air Quality projections

2013

8 Anthropogenic and Natural Radiative Forcing

SPM Summary for Policymakers

RF as driven by emissions of indirect GHGases !



2013

11 Near-term Climate Change: Projections and Predictability

Future surface O_3 assessed

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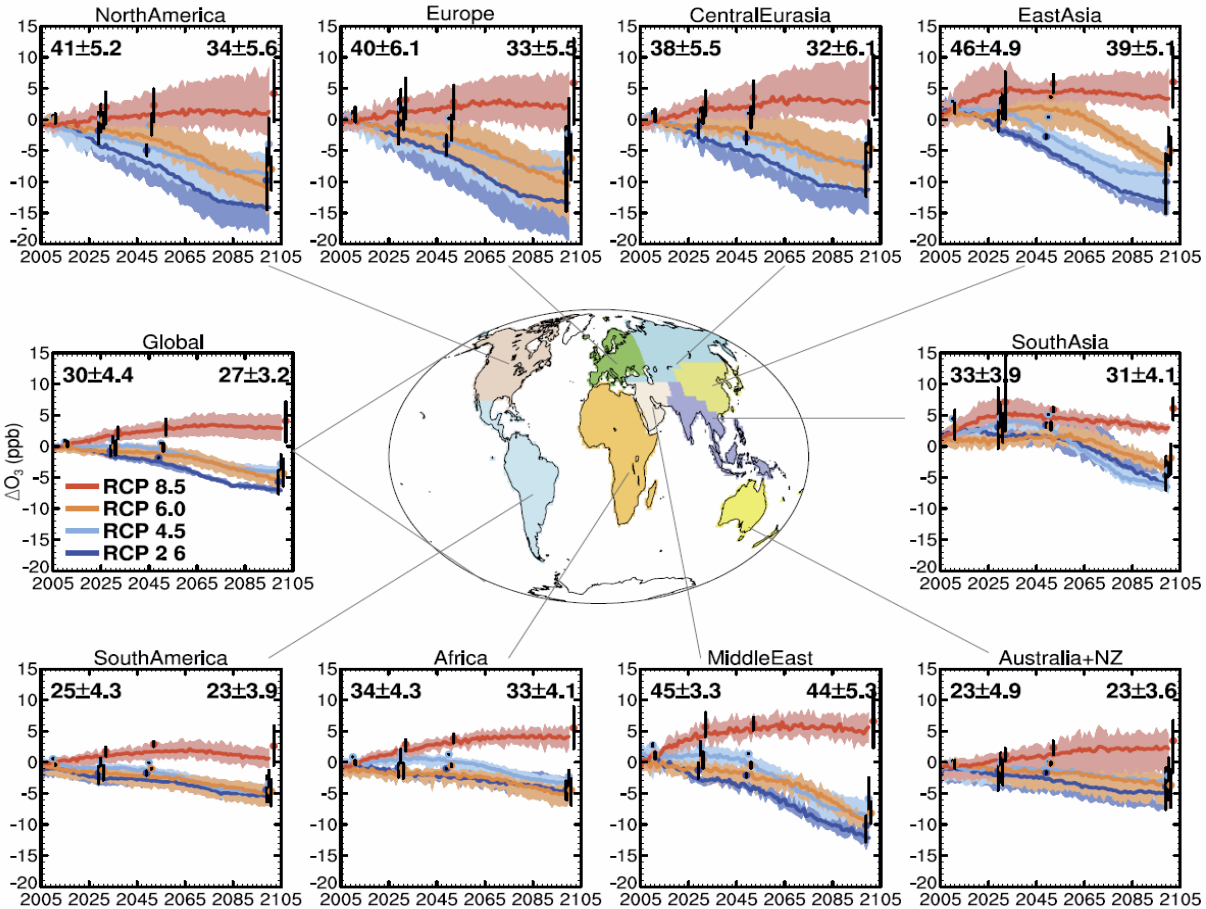

Figure 11.23a | Projected changes in annual mean surface O_3 (ppb mole fraction) from 2000 to 2100 following the RCP scenarios

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11 Near-term Climate Change: Projections and Predictability

Uncertainty in both
emissions scenarios &
future CH_4
were evaluated.

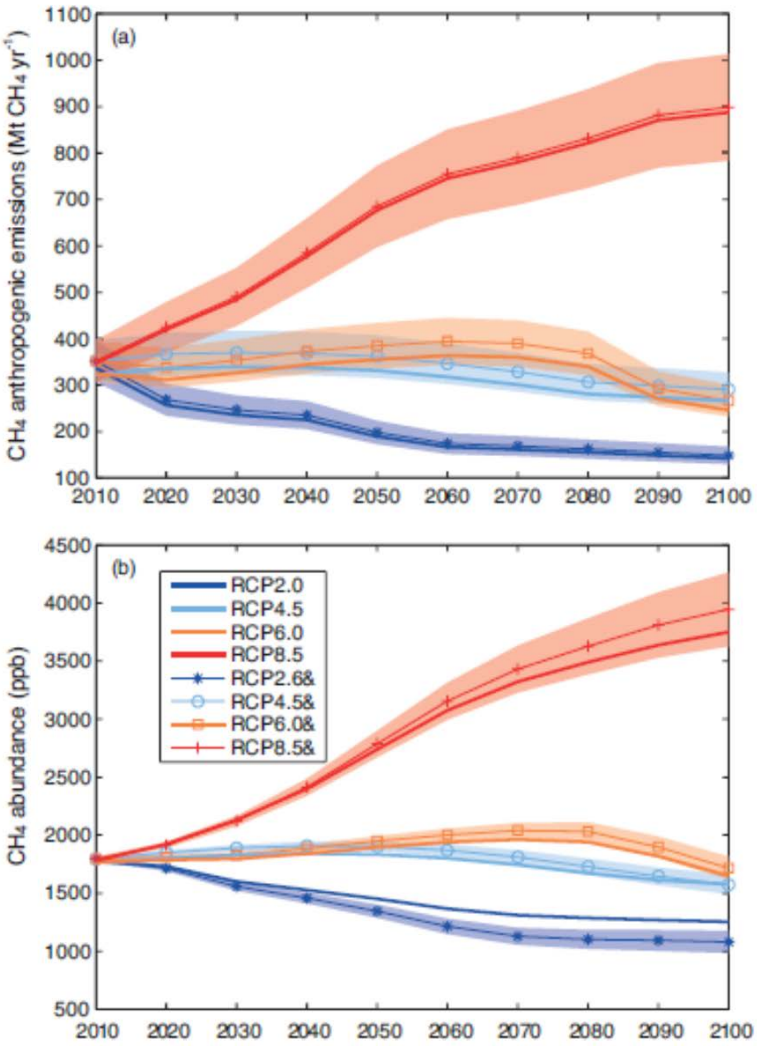
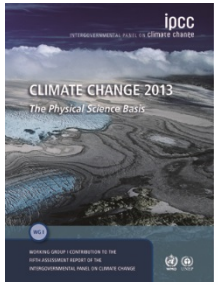


Figure 11.21 | Projections for CH_4 (a) anthropogenic emissions ($MtCH_4\ yr^{-1}$) and (b) atmospheric abundances (ppb) for the four RCP scenarios (2010–2100). Natural emissions in 2010 are estimated to be 202 ± 35 $MtCH_4\ yr^{-1}$ (see Chapter 8). The thick solid lines show the published RCP2.6 (light blue), RCP4.5 (dark blue), RCP6.0 (orange) and



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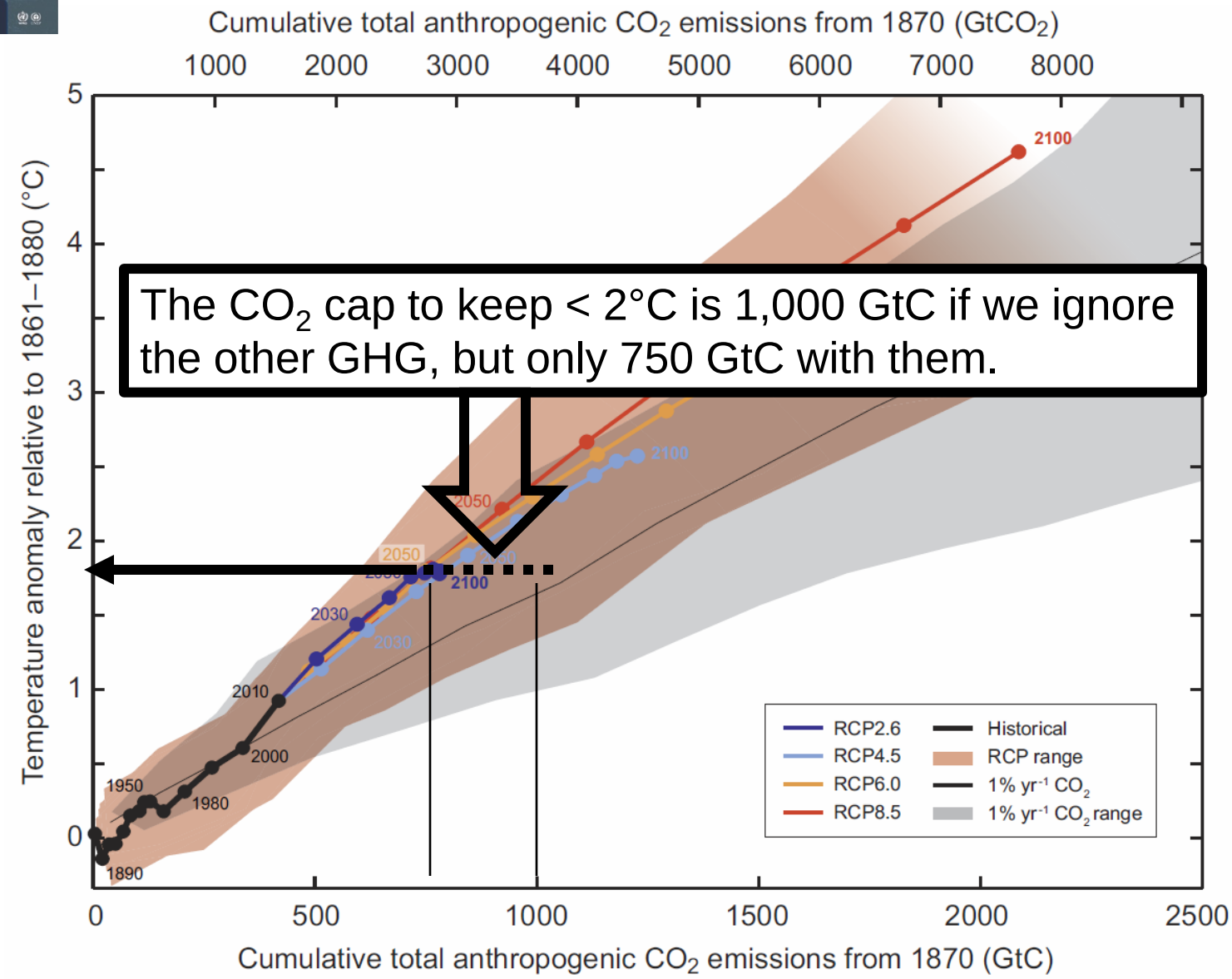
Why do we care about atmospheric chemistry for climate? ***CH_4, tropospheric O_3, N_2O, … do matter***



The CO_2 cap to keep < 2°C is 1,000 GtC if we ignore the other GHG, but only 750 GtC with them.

Forecast for global atmospheric chemistry in climate assessments ?

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Ice off the western Antarctic Peninsula in March. Australia's science agency is laying off 275 scientists as it shifts its focus away from climate research and toward more commercial projects.

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