Geochemistry of other trace gases (non-CO2 greenhouse gase

12.340 Global Warming Science
March 20, 2012
Dan Cziczo

Reading: Archer, Chapter 4

Today's Class

- recap the atmosphere and greenhouse concept
- The other greenhouse gases
- The case of CFCs

Recap

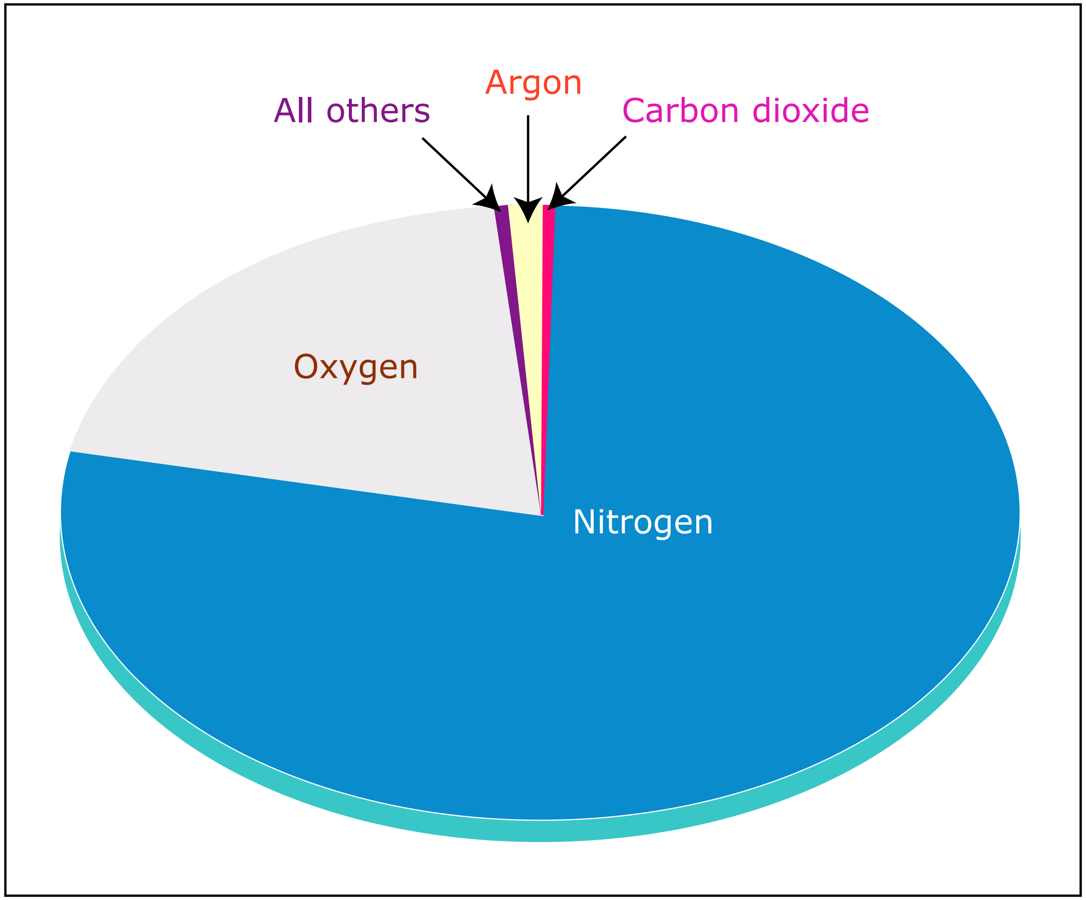


Image by MIT OpenCourseWare.

Early Atmosphere

Probably H_2, He

- Likely lost to space early

Later Atmosphere

- Volcanic out gassing + impacts : H_2O, CO_2, SO_2, CO, S_2, Cl_2 N_2, H_2, NH_3, and CH_4

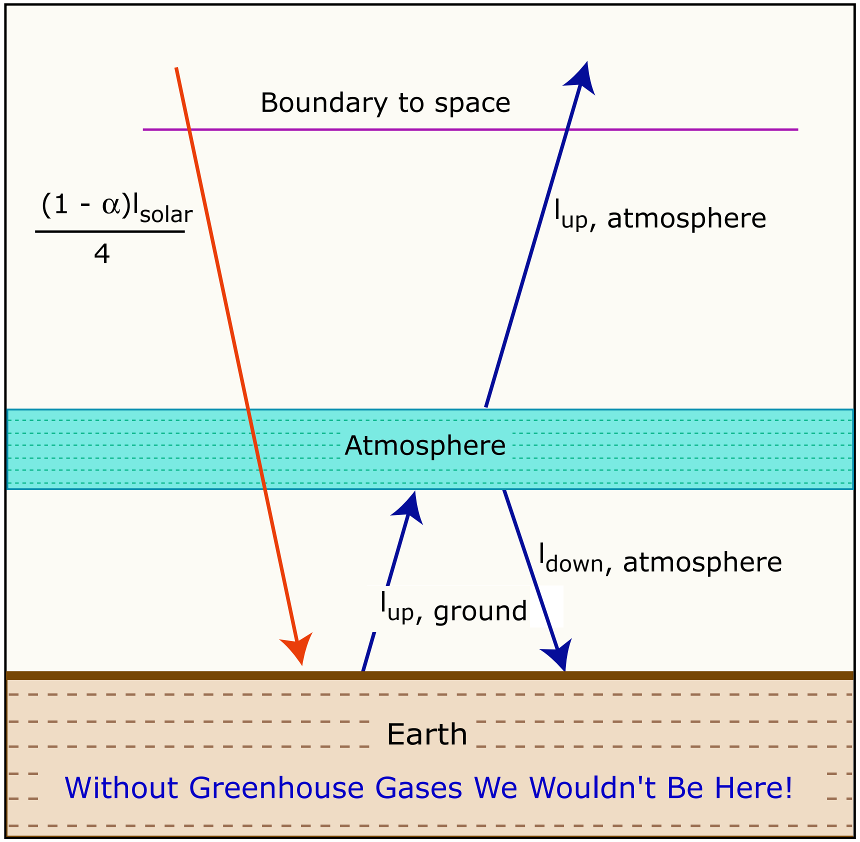
Life

- O /CO_2 balance

Everything else

<< 1%

Lutgens and Tarbuck, *The Atmosphere*, 8th edition



Planet	α (%)	T (K)	$T_{observed}$ (K)	$T_{1\ layer}$ (K)	I_{solar} (Wm^{-2})
Venus	71	240	700	285	2600
Earth	33	251	295	303	1350
Mars	17	216	240	259	600

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Modern CO2

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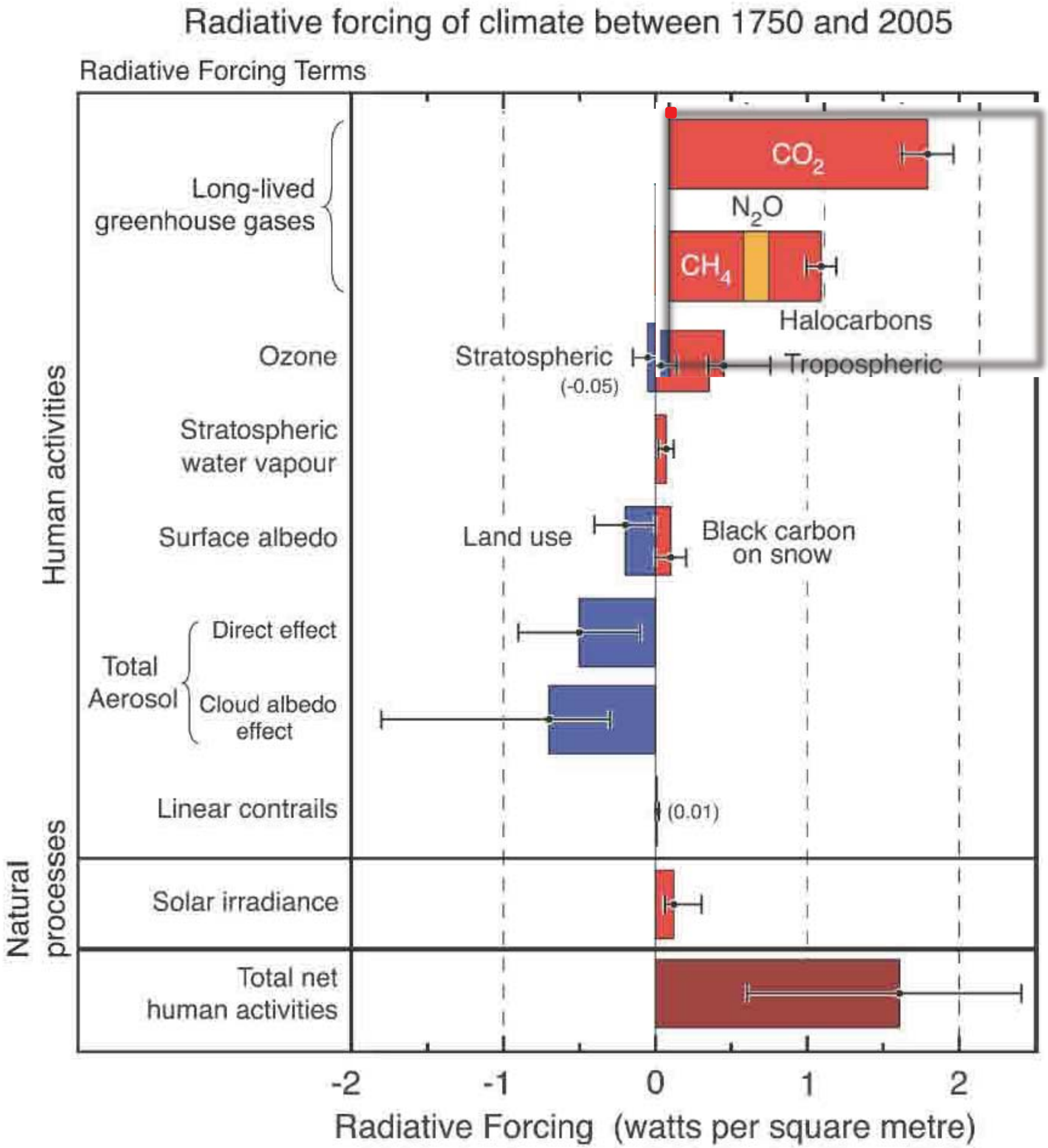


Solar Irradiance ~ 1350 W/m^2

(more in Lecture 15)

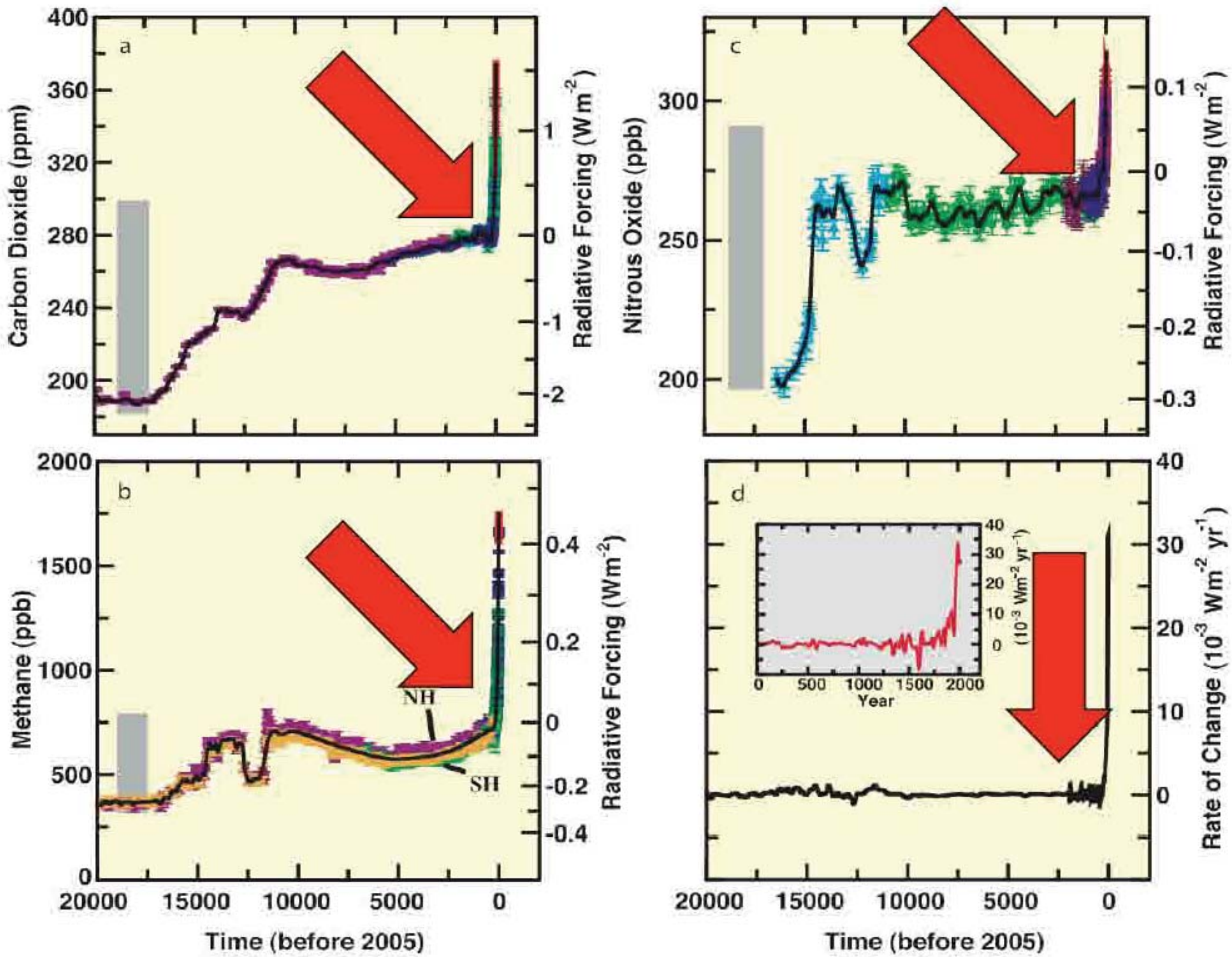
Climate Change 2007: The Physical Science Basis. Working Group I Contribution to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, FAQ 2.1, Figure 2. Cambridge University Press. Used with permission.

IPCC

No Models! (ok, a little modeling)

(more in Lecture 15,17,18)

Murphy et al. JGR 2009



The concentrations and radiative forcing by (a) carbon dioxide (CO_2), (b) methane (CH_4), (c) nitrous oxide (N_2O) and (d) the rate of change in their combined radiative forcing over the last 20,000 years reconstructed from Antarctic and Greenland ice and firn data (symbols) and direct atmospheric measurements (panels a,b,c, red lines). The grey bars show the reconstructed ranges of natural variability for the past 650,000 years. The rate of change in radiative forcing (panel d, black line) has been computed from spline fits to the concentration data. The negative rate of change in forcing around 1600 shown in the higher-resolution inset in panel d results from a CO_2 decrease of about 10 ppm in the ice core record.

Climate Change 2007: The Physical Science Basis. Working Group I Contribution to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Figure 6.4. Cambridge University Press. Used with permission.

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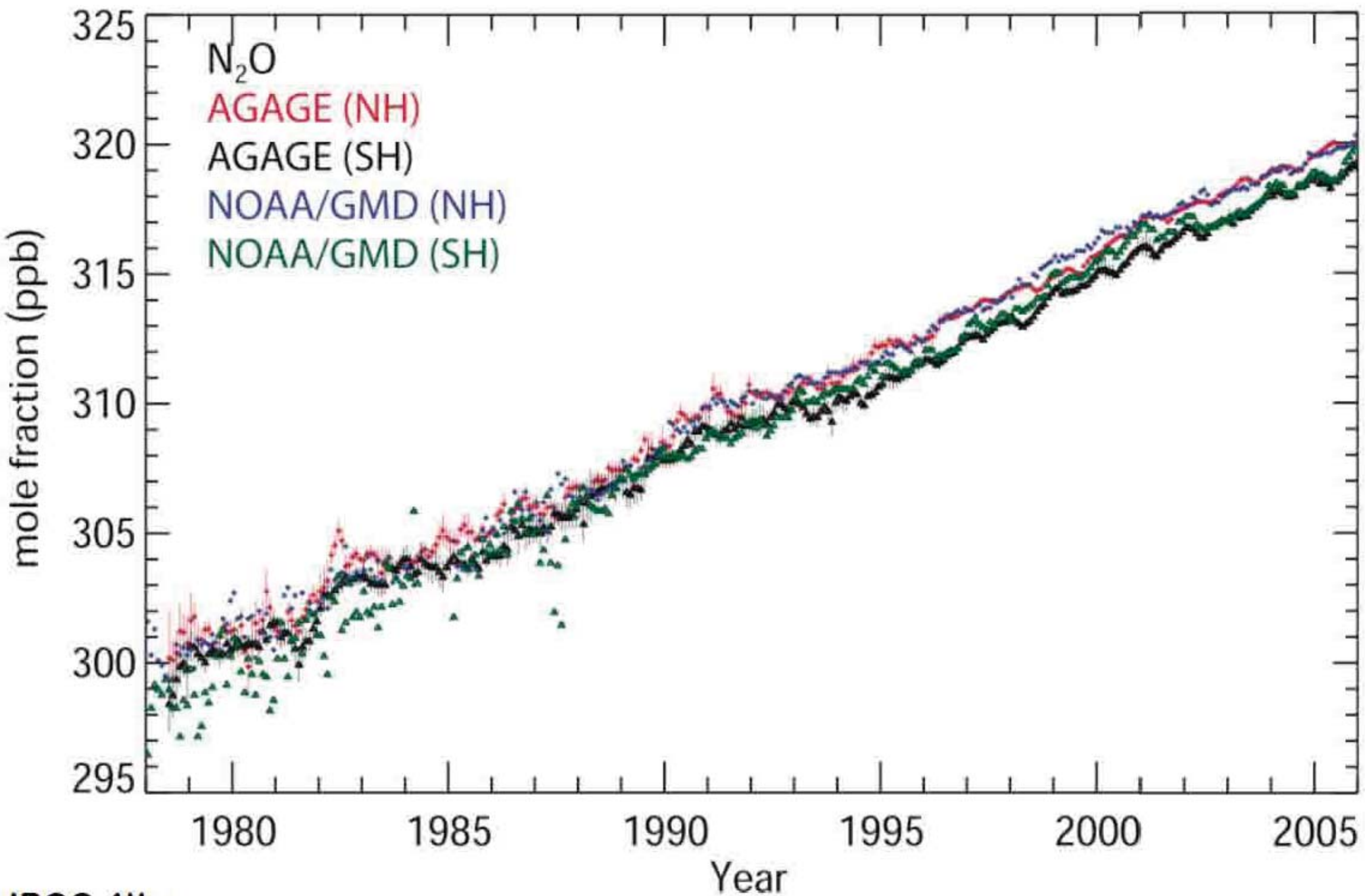
CH_4 and Nitrous Oxide Global Emissions - IPCC

TRENDS IN NITROUS OXIDE



Ref: IPCC 4th Assessment, Summary for Policymakers, Feb. 2, 2007

$$dM/dt = E - M/T; \text{ Lifetime } (T)$$

$$0.0025 = 0.0105 - 1/125$$
$$= 0.0105 - 0.0080$$

Climate Change 2007: The Physical Science Basis. Working Group I Contribution to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Figure 2.5. Cambridge University Press. Used with permission.

What's Strange About methane?

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GEOPHYSICAL RESEARCH LETTERS, VOL. 35, L22805, doi:10.1029/2008GL036037, 2008

Renewed growth of atmospheric methane

M. Rigby,[1] R. G. Prinn,[1] P. J. Fraser,[2] P. G. Simmonds,[3] R. L. Langenfelds,[2] J. Huang,[1] D. M. Cunnold,[4] L. P. Steele,[2] P. B. Krummel,[2] R. F. Weiss,[5] S. O'Doherty,[3] P. K. Salameh,[5] H. J. Wang,[4] C. M. Harth,[5] J. Mühle,[5] and L. W. Porter[6,7]

HOW CAN WE COMPARE EMISSION REDUCTIONS OF NON-CO_2 GASES TO CO_2 FOR POLICY PURPOSES?

THE KYOTO PROTOCOL HAS ADOPTED GLOBAL WARMING POTENTIALS TO DEFINE THE "EXCHANGE RATES" BETWEEN GASES FOR EMISSION REDUCTION PURPOSES

Global Warming Potentials (GWPs)

$$GWP = \frac{\int_0^T I_{gas} M_{gas}\, dt}{\int_0^T I_{CO_2} M_{CO_2}\, dt}$$

I_{gas} = instantaneous radiative forcing by gas at time t [depends on basic molecular properties and on atmospheric composition (gases, clouds, aerosols)]

M_{gas} = amount of added gas still remaining at time t [depends on lifetime of the gas, which in turn usually depends on amounts of the gas itself and of other gases (indirect effects)]

T = time horizon for integration [gases with lifetimes (longer/shorter) than CO_2 have GWPs (increasing/decreasing) with T]

Notes

1. Corrections must be made to account for effects of added gas on amounts of other greenhouse gases (e.g., effects of added CH_4 on O_3 and H_2O)
2. M_{CO_2} depends on assumptions regarding oceanic and terrestrial CO_2 sinks

TABLE 3: Direct Global Warming Potentials (GWPs) relative to carbon dioxide (for gases for which the lifetimes have been adequately characterised). GWPs are an index for estimating relative global warming contribution due to atmospheric emission of a kg of a particular greenhouse gas compared to emission of a kg of carbon dioxide. GWPs calculated for different time horizons show the effects of atmospheric lifetimes of the different gases . [Based upon Table 6.7]

Gas		Lifetime (years)	Global Warming Potential (Time Horizon in years) 20 yrs	100 yrs	500 yrs
Carbon dioxide	CO_2		1	1	1
Methane[a]	CH_4	12.0[b]	62	23	7
Nitrous oxide	N_2O	114[b]	275	296	156
Hydrofluorocarbons					
HFC-23	CHF_3	260	9400	12000	10000
HFC-32	CH_2F_2	5.0	1800	550	170
HFC-41	CH_3F	2.6	330	97	30
HFC-125	CHF_2CF_3	29	5900	3400	1100
HFC-134	CHF_2CHF_2	9.6	3200	1100	330
HFC-134a	CH_2FCF_3	13.8	3300	1300	400
HFC-143	CHF_2CH_2F	3.4	1100	330	100
HFC-143a	CF_3CH_3	52	5500	4300	1600
HFC-152	CH_2FCH_2F	0.5	140	43	13
HFC-152a	CH_3CHF_2	1.4	410	120	37
HFC-161	CH_3CH_2F	0.3	40	12	4
HFC-227ea	CF_3CHFCF_3	33	5600	3500	1100
HFC-236cb	$CH_2FCF_2CF_3$	13.2	3300	1300	390
HFC-236ea	CHF_2CHFCF_3	10	3600	1200	390
HFC-236fa	$CF_3CH_2CF_3$	220	7500	9400	7100
HFC-245ca	$CH_2FCF_2CHF_2$	5.9	2100	640	200
HFC-245fa	$CHF_2CH_2CF_3$	7.2	3000	950	300
HFC-365mfc	$CF_3CH_2CF_2CH_3$	9.9	2600	890	280
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	15	3700	1500	470
Fully fluorinated species					
SF_6		3200	15100	22200	32400
CF_4		50000	3900	5700	8900
C_2F_6		10000	8000	11900	18000
C_3F_8		2600	5900	8600	12400
C_4F_{10}		2600	5900	8600	12400
c-C_4F_8		3200	6800	10000	14500
C_5F_{12}		4100	6000	8900	13200
C_6F_{14}		3200	6100	9000	13200
Ethers and Halogenated Ethers					
CH_3OCH_3		0.015	1	1	<<1
HFE-125	CF_3OCHF_2	150	12900	14900	9200
HFE-134	CHF_2OCHF_2	26.2	10500	6100	2000
HFE-143a	CH_3OCF_3	4.4	2500	750	230
HCFE-235da2	$CF_3CHClOCHF_2$	2.6	1100	340	110
HFE-245fa2	$CF_3CH_2OCHF_2$	4.4	1900	570	180
HFE-254cb2	$CHF_2CF_2OCH_3$	0.22	99	30	9
HFE-7100	$C_4F_9OCH_3$	5.0	1300	390	120
HFE-7200	$C_4F_9OC_2H_5$	0.77	190	55	17
H-Galden 1040x	$CHF_2OCF_2OC_2F_4OCHF_2$	6.3	5900	1800	560
HG-10	$CHF_2OCF_2OCHF_2$	12.1	7500	2700	850
HG-01	$CHF_2OCF_2CF_2OCHF_2$	6.2	4700	1500	450

[a] The methane GWPs include an indirect contribution from strato[illegible] H_2O a[illegible]roductio[illegible]
[b] The values for methane and nitrous oxide are adjustment times, [illegible] incorpo[illegible] indirect effects of emission of each gas on its own lifetime.

http://www.ipcc.ch

RGP 2/02_12.848_IPCCwg1techsum.pg.47.eps

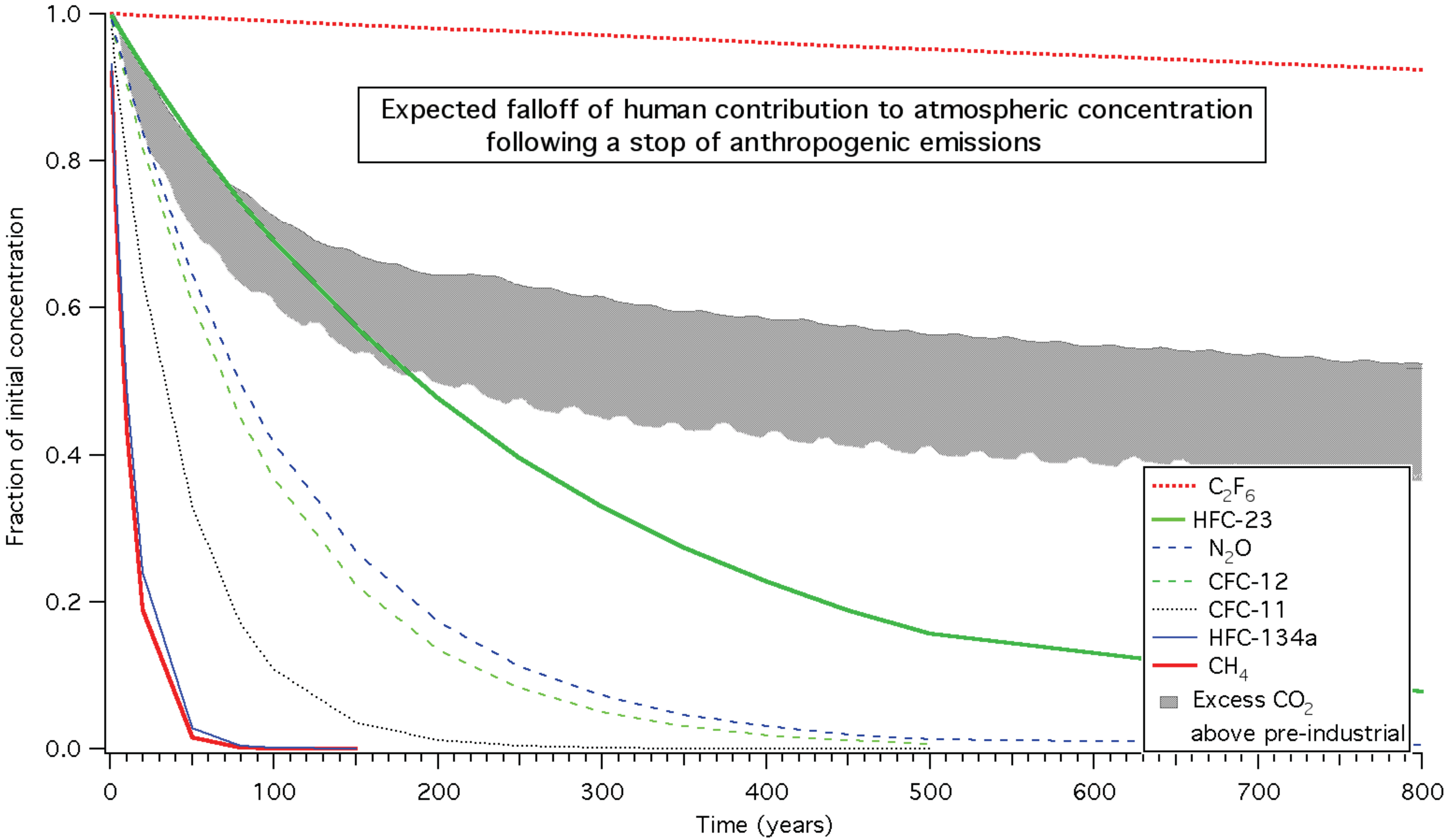
GWP's VERY DEPENDENT ON THE GAS's INSTANTANEOUS RADIATIVE FORCING, LIFETIME* & CHOSEN TIME HORIZON

KYOTO PROTOCOL ADOPTS A 100-YEAR TIME HORIZON

IS THIS SCIENTIFICALLY JUSTIFIABLE? (e.g. methane)

***Note special case when gas lifetime similar to CO_2 lifetime (e.g. N_2O)**

What's Special About Carbon Dioxide ?



(1) $CO_2 + H_2O$ <-> $H^+ + HCO_3^-$ Initial step

(2) $CO_2 + H_2O + CO_3^{-2}$ <-> $2HCO_3^-$ ~100,000 years

Archer (many papers); review in Solomon et al., PNAS, 2009; Revelle and Suess 1957

Why?

-Climate system lags (ocean heat uptake)

-Nonlinear spectroscopy for some, where warming doesn't follow the concentration decay (CO_2, CH_4).

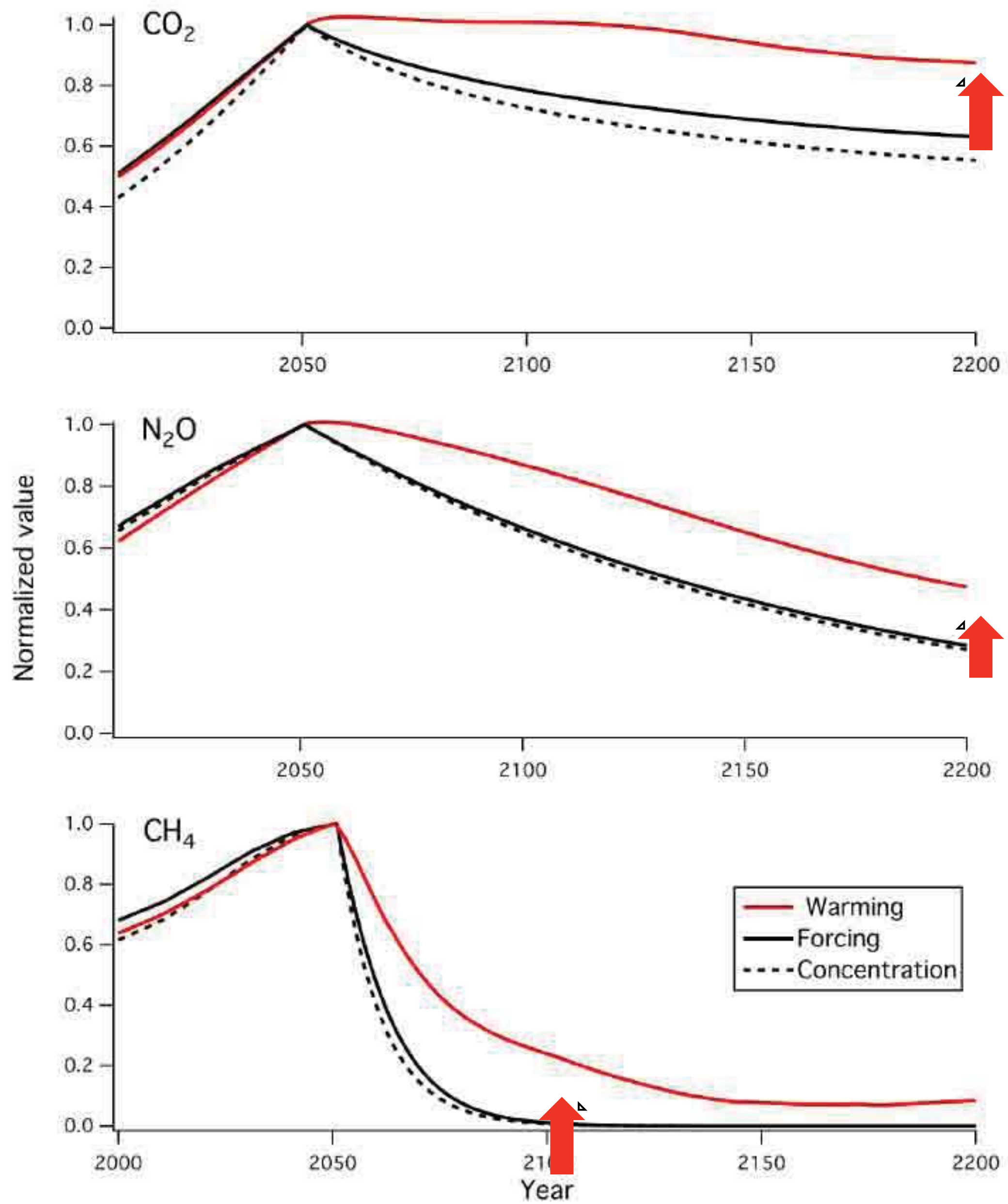


Image courtesy of Susan Solomon. Used with permission.

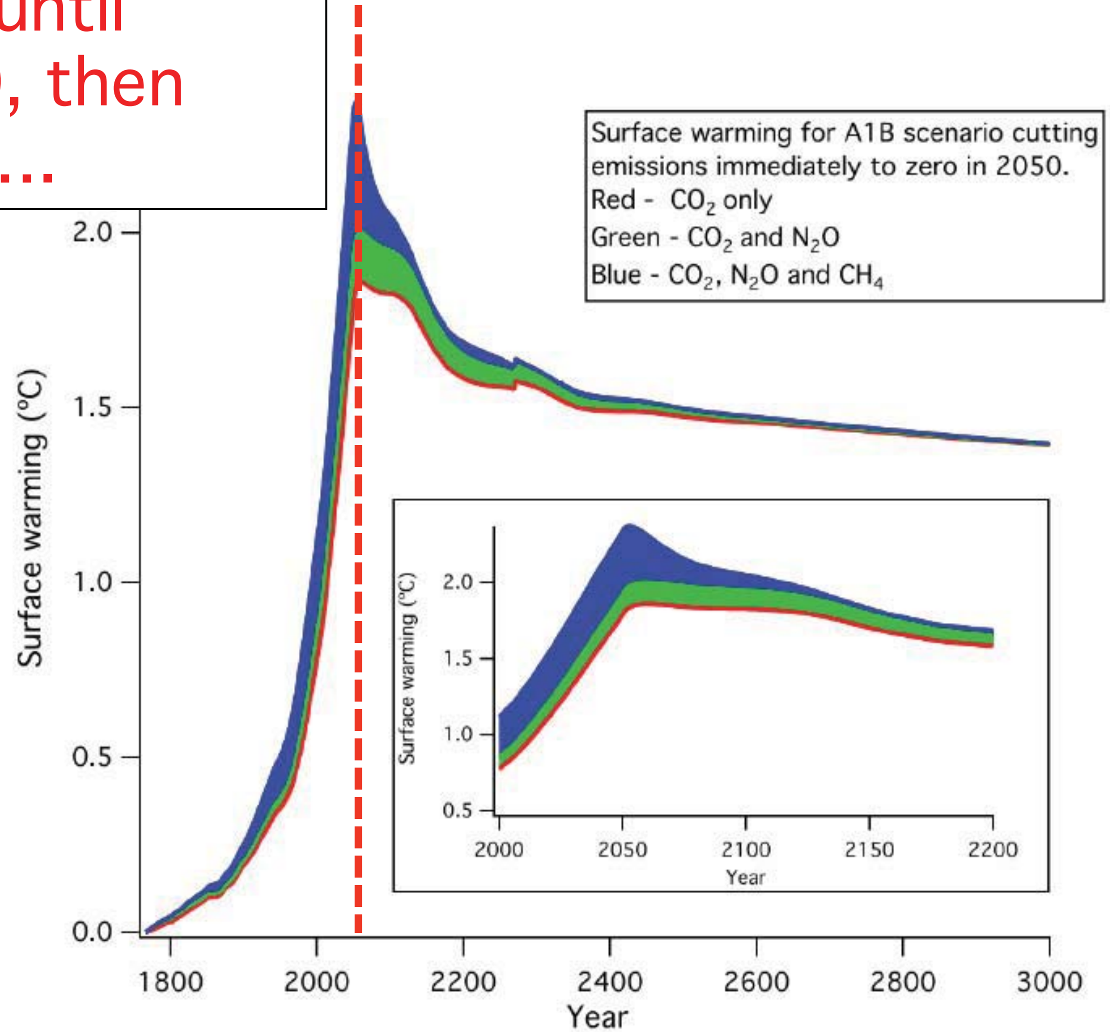
Bern 2.5CC EMIC runs - Solomon et al., PNAS, 2010.

Emit until 2050, then stop....

Lifetime of N_2O ≈ 110 years

Lifetime of CH_4 ≈ 10 years

Warming due to CO_2 persists for more than 1000 years; for N_2O several hundred years; for methane many decades.



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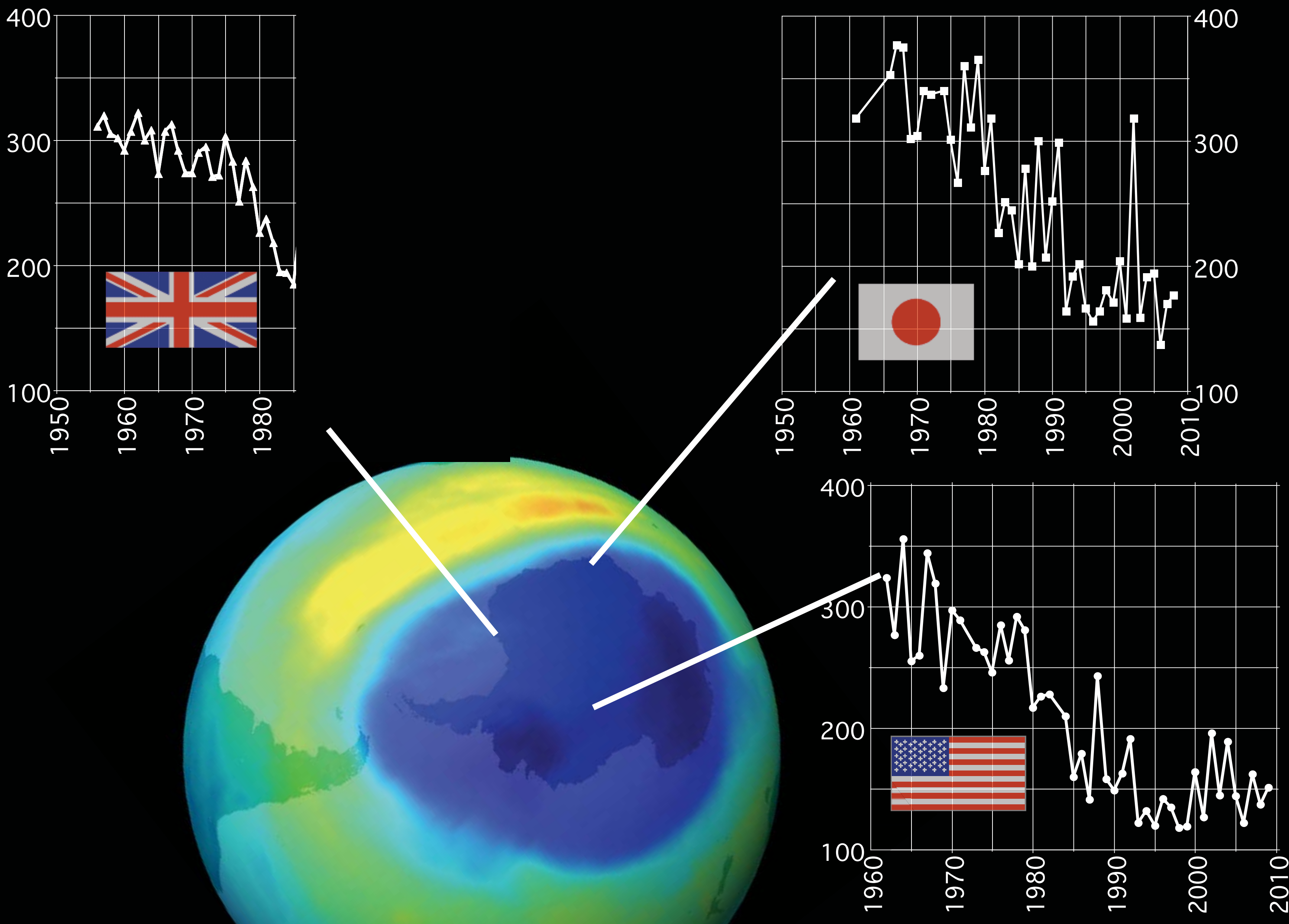
Bern 2.5CC EMIC runs - Solomon et al., PNAS, 2010.

Chlorofluorocarbon = CFC

Originally used as a fire fighting material (replacement of oxygen), later used in foam, a refrigerant, solvent, and aerosol propellant

Banned due to ozone destruction…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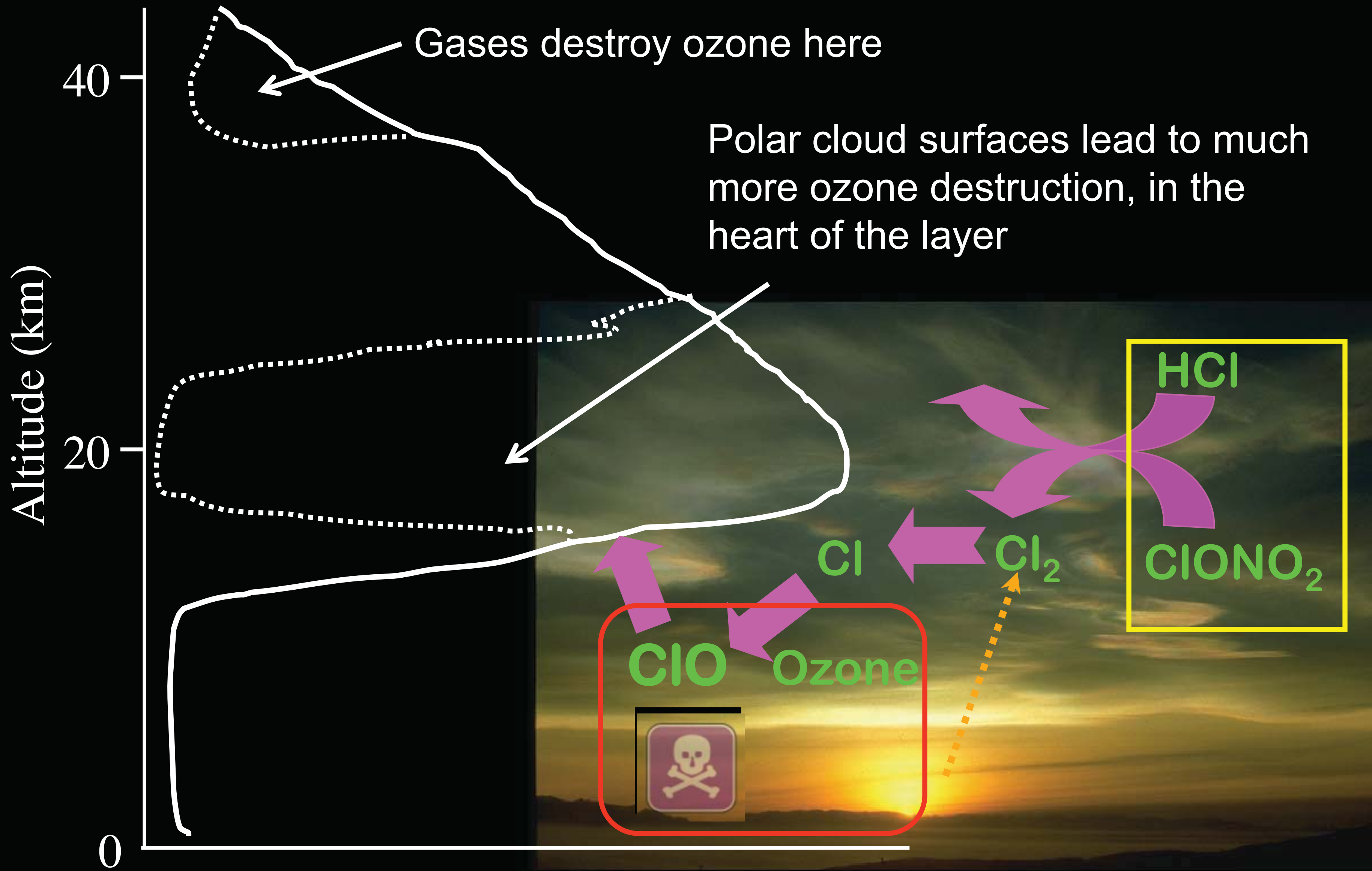
Courtesy



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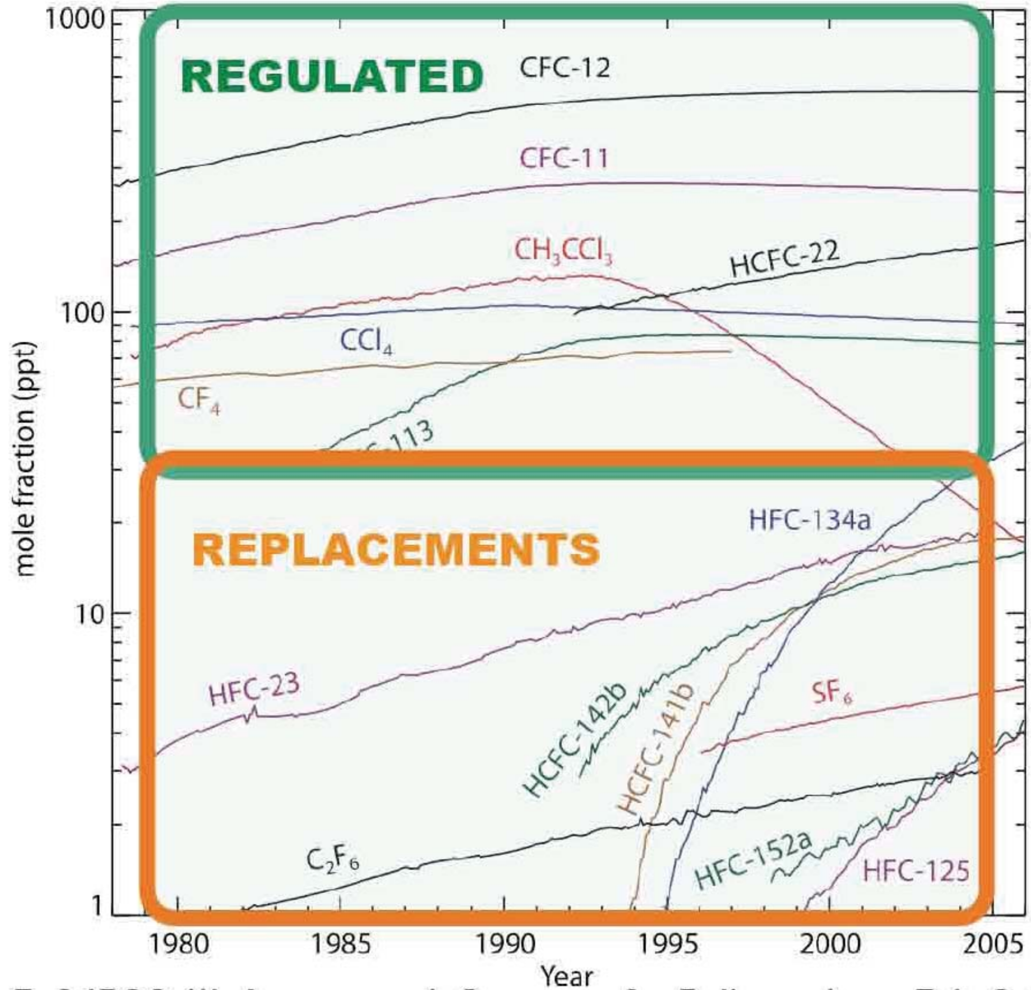
Amount of ozone

Activated for ozone loss

Reservoirs

Sun+Cold: Both Needed

HCFCs and HFCs



Ref: IPCC 4th Assessment, Summary for Policymakers, Feb. 2, 2007

Climate Change 2007: The Physical Science Basis. Working Group I Contribution to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Figure 2.6. Cambridge University Press. Used with permission.

CFCs are strong absorbers of infrared light, and *directly* contribute to global warming {CFC physics}

Greenhouse Effect Due to Chlorofluorocarbons:

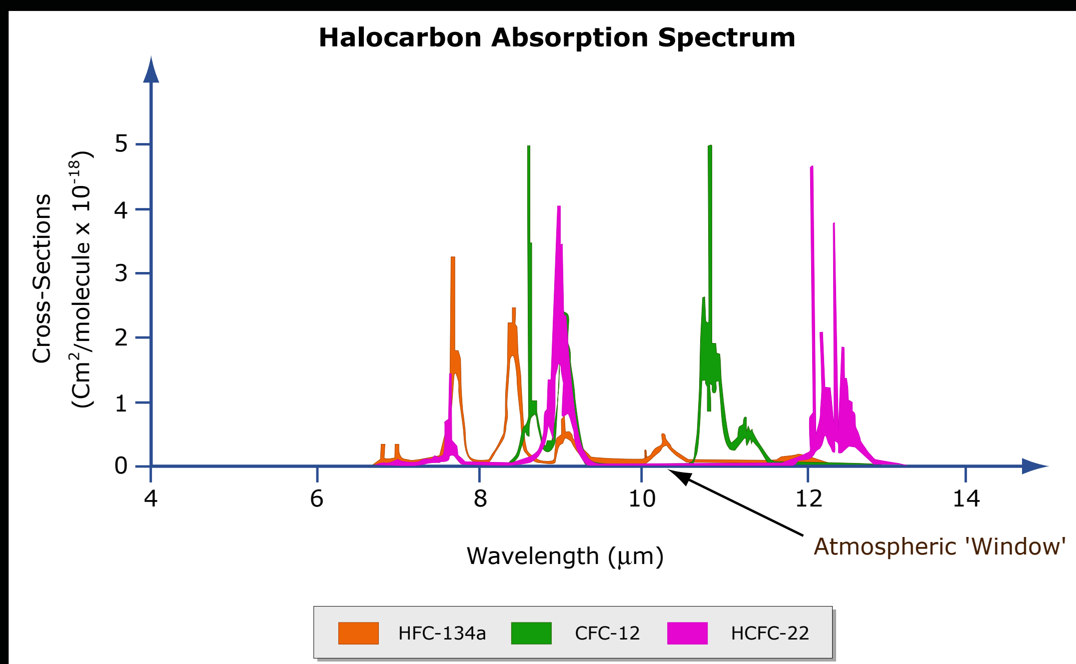
Climatic Implications

Abstract -

The infrared bands of chlorofluorocarbons and chlorocarbons enhance the atmospheric greenhouse effect. This enhancement may lead to an appreciable increase in the global surface temperature if the atmospheric concentrations of these compounds reach values of the order of 2 parts per billion.

Ramanathan, Science, 1975.

Image by MIT OpenCourseWare.



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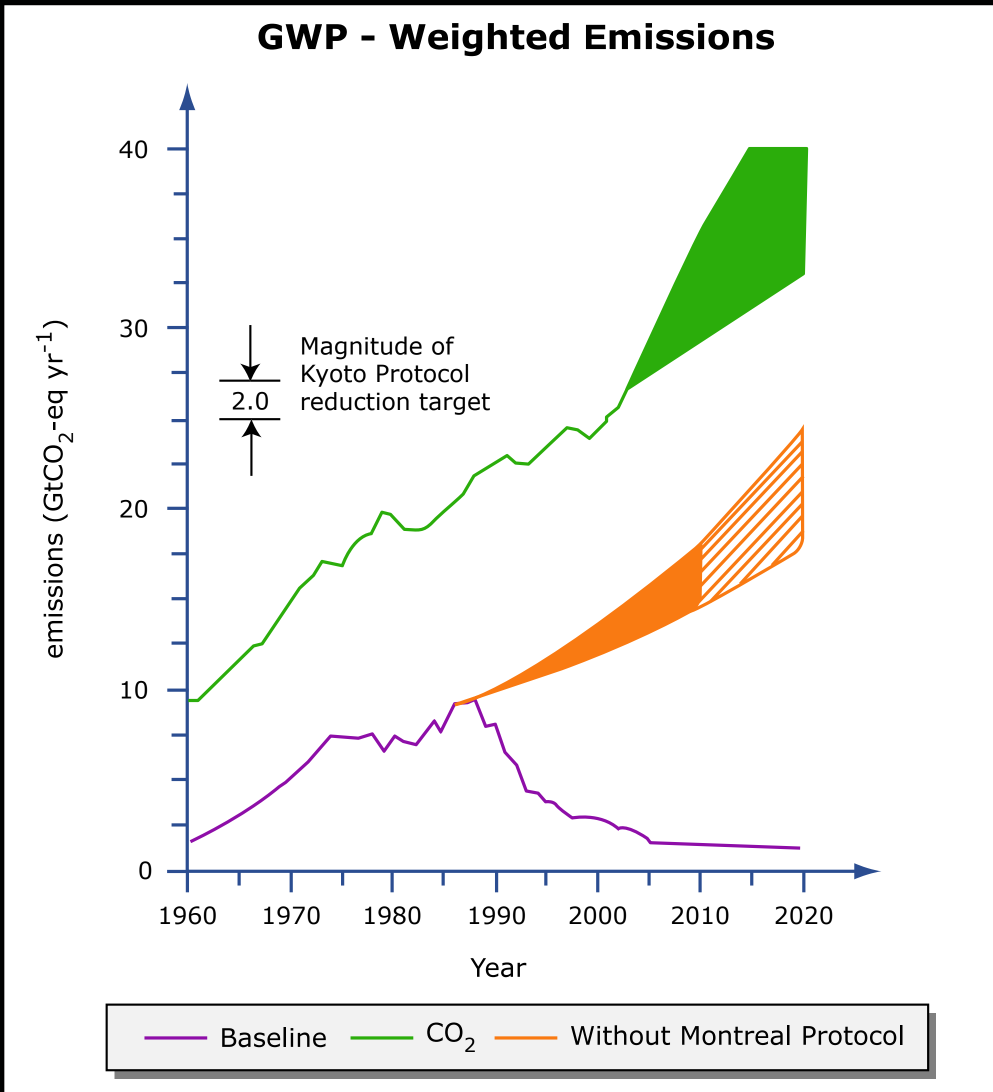
Benefits of Montreal Protocol for Climate



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- CO_2 emissions
- World avoided by the Montreal Protocol?
- Reduction Montreal Protocol of ~11 $GtCO_2$-eq/yr

➔5-6 times global Kyoto target

Role of ozone depletion cooling due to CFCs? Could reduce this by perhaps a third but….

Global Warming Potentials				
Designation	Chemical Formula	20 years	100 years	500 years
CFC-11	$CFCl_3$	5000	4000	1400
CFC-12	CF_2Cl_2	7900	8500	4200
CFC-13	$CClF_3$	8100	11700	13600
CFC-113	$C_2F_3Cl_3$	5000	5000	2300
CFC-114	$C_2F_4Cl_2$	6900	9300	8300
CFC-115	C_2F_5Cl	6200	9300	13000
H-1305	$CBrF_3$	6200	5600	2200
HCFC-22	CF_2HCl	4300	1700	520
HCFC-141b	$C_2FH_3Cl_2$	1800	630	200
HCFC-142b	$C_2F_2H_3Cl$	4200	2000	630
HCFC-123	C_2F_3HCl2	300	93	29
HCFC-124	C_2F_4HCl	1500	480	150
HCFC-225ca	$C_3F_5HCl_2$	550	170	52
HCFC-225cb	$C_3F_5HCl_2$	1700	530	170
Carbon tetrachloride	CCl_4	2000	1400	500
Methyl chloroform	CH_3CCl_3	360	110	35

Source: Scientific Assessment of Ozone Depletion (1994): Chapter 13, "Ozone Depleting Potentials, Global Warming Potentials and Future Chlorine/Bromine Loading". UNEP, February 1995.

HFC-125	CHF_2CF_3	29	5900	3400	1100
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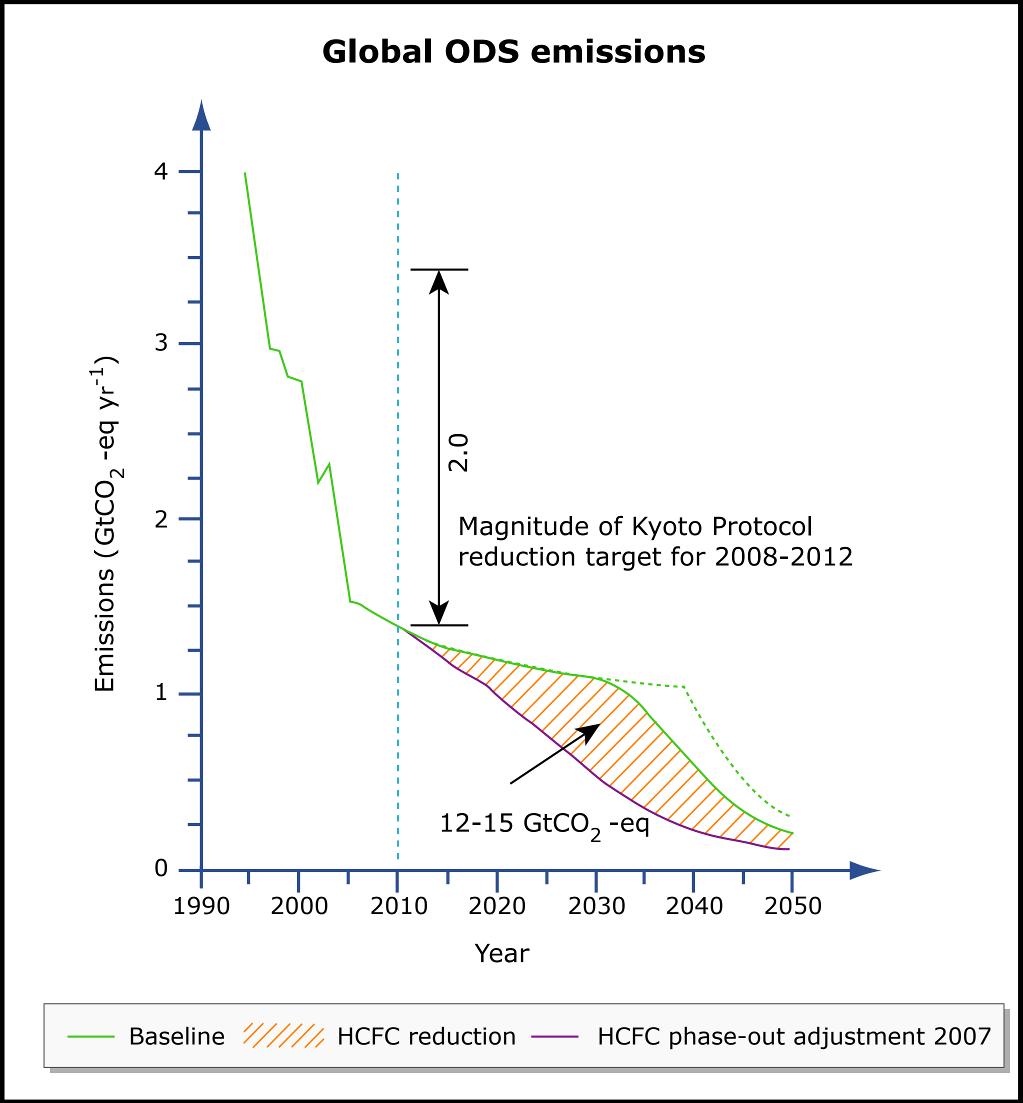
[b] The values for methane and nitrous oxide are adjustment times, [illegible] incorpor[illegible] indirect effects of emission of each gas on its own lifetime

Climate Change 2007: The Physical Science Basis. Working Group I Contribution to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Table TS.3. Cambridge University Press. Used with permission.

Montreal Sep 2007 adjustment: HCFC early phase-out



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Reduction in emissions:

HCFCs 'transition' speedup

12-15 $GtCO_2$-eq potential reduction if replaced with low-GWP alternatives or reduced through conservation/recycling.

Recap of Today's Class

- recap the atmosphere and greenhouse concept

The other greenhouse gases

The case of CFCs

12.340 Global Warming Science
Spring 2012