
Part I

Possible Causes of Climate Change

The Role of Atmospheric Gases in Global Warming

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1. INTRODUCTION

If the general public in the developed world is confused about what the greenhouse effect is, what the important greenhouse gases are, and whether greenhouse gases really are the predominant cause of the recent rise in temperature of the earth's atmosphere, it is hardly surprising. Nowadays, statements by one scientist are often immediately refuted by another, and both tend to state their claims with almost religious fervour. Furthermore, politicians and the media have not helped. It is only 14 a (years) ago that the newly appointed Secretary of State for the Environment in the United Kingdom made the cardinal sin of confusing the greenhouse effect with ozone depletion by saying they had the same scientific causes. (In retrospect, John Gummer was closer to the truth than he realised, in that one class of chemicals, the chlorofluorocarbons (CFCs), are both the principal cause of ozone depletion and are major greenhouse gases, but these two facts are scientifically unrelated.) Furthermore, to many, even in the respectable parts of the media, 'greenhouse gases' are two dirty words. In fact, nothing could be further from the truth, in that there has always been a greenhouse effect operative in the earth's atmosphere.

Without it we would inhabit a very cold planet, and not exist in the hospitable temperature of 290–300 K.

The purpose of this opening chapter of this book is to explain in simple terms what the greenhouse effect is, what its origins are and what the properties of greenhouse gases are. I will restrict this chapter to an explanation of the physical chemistry of greenhouse gases and the greenhouse effect, and not delve too much into the politics of ‘what should or should not be done’. However, one simple message to convey at the onset is that the greenhouse effect is not just about concentration levels of carbon dioxide (CO_2), and it is too simplistic to believe that all our problems will be solved, if we can reduce CO_2 concentrations by $x\%$ in y years. Shine [1] has also commented many times that there is much more to the greenhouse effect than carbon dioxide levels.

2. ORIGIN OF THE GREENHOUSE EFFECT: ‘PRIMARY’ AND ‘SECONDARY’ EFFECTS

The earth is a planet in dynamic equilibrium, in that it continually absorbs and emits electromagnetic radiation. It receives ultra-violet and visible radiation from the sun, it emits infra-red radiation and energy balance says that ‘energy in’ must equal ‘energy out’ for the temperature of the planet to be constant. This equality can be used to determine what the average temperature of the planet should be. Both the sun and the earth are black-body emitters of electromagnetic radiation. That is, they are masses capable of emitting and absorbing all frequencies (or wavelengths) of electromagnetic radiation uniformly. The distribution curve of emitted energy per unit time per unit area versus wavelength for a black body was worked out by Planck in the first part of the twentieth century, and is shown pictorially in Fig. 1. Without mathematical detail, two points are relevant. First, the total energy emitted per unit time integrated over all wavelengths is proportional to $(T/\text{K})^4$. Second, the wavelength of the maximum in the emission distribution curve varies inversely with (T/K) , that is, $\lambda_{\text{max}} \propto (T/\text{K})^{-1}$. These are Stefan’s and Wien’s

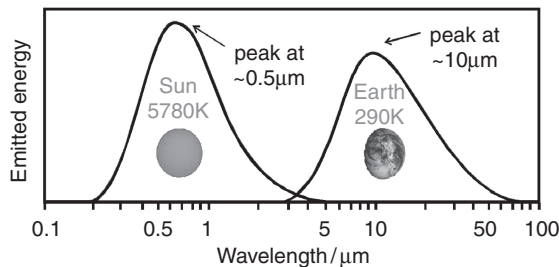


FIGURE 1 Black-body emission curves from the sun ($T \sim 5780$ K) and the earth ($T \sim 290$ K), showing the operation of Wien’s Law that $\lambda_{\text{max}} \propto (1/T)$. The two graphs are not to scale. (See Color Plate 1).

Laws, respectively. Comparing the black-body curves of the sun and the earth, the sun emits UV/visible radiation with a peak at ca. 500 nm characteristic of $T_{\text{sun}} = 5780$ K. The temperature of the earth is a factor of 20 lower, so the earth's black-body emission curve peaks at a wavelength which is 20 times longer or ca. 10 μm . Thus the earth emits infra-red radiation with a range of wavelengths spanning ca. 4–50 μm , with the majority of the emission being in the range 5–25 μm (or 400–2000 cm^{-1}).

The solar flux energy intercepted per second by the earth's surface from the sun's emission can be written as $F_s(1-A)\pi R_e^2$, where F_s is the solar flux constant outside the Earth's atmosphere ($1368 \text{ J}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$), R_e is the radius of the Earth (6.38×10^6 m), and A is the earth's albedo, corresponding to the reduction of incoming solar flux by absorption and scattering of radiation by aerosol particles (average value 0.28). The infra-red energy emitted per second from the earth's surface is $4\pi R_e^2 s T_e^4$, where s is Stefan's constant ($5.67 \times 10^{-8} \text{ J}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{-4}$) and $4\pi R_e^2$ is the surface area of the earth. At equilibrium, the temperature of the earth, T_e , can be written as:

$$T_e = \left[\frac{F_s(1-A)}{4s} \right]^{1/4} \quad (1)$$

Using the data above yields a value for T_e of ca. 256 K. Mercifully, the average temperature of the earth is not a Siberian -17°C , otherwise life would be a very unpleasant experience for the majority of humans on this planet. The reason why our planet has a hospitable higher average value of ca. 290 K is the greenhouse effect. For thousands of years, absorption of some of the emitted infra-red radiation by molecules in the earth's atmosphere (mostly CO_2 , O_3 and H_2O) has trapped this radiation from escaping out of the earth's atmosphere (just as a garden greenhouse operates), some is re-radiated back towards the earth's surface, thereby causing an elevation in the temperature of the surface of the earth. Thus, it is the greenhouse effect that has maintained our planet at this average temperature, and for this fact we should all be very grateful! This phenomenon is often called the 'primary' greenhouse effect. It is, therefore, a myth to portray all aspects of the greenhouse effect as bad news; it is the reverse that is true.

Evidence for the presence of greenhouse gases absorbing infra-red radiation in the atmosphere comes from satellite data. Figure 2 shows data collected by the Nimbus 4 satellite circum-navigating the earth at an altitude outside the earth's troposphere ($0 < \text{altitude}, h < 10$ km) and stratosphere ($10 < h < 50$ km). The infra-red emission spectrum in the range 6–25 μm escaping from earth represents a black-body emitter with a temperature of ca. 290 K, with absorptions (i.e., dips) between 12 and 17 μm , around 9.6 μm , and $\lambda < 8$ μm . These wavelengths correspond to infra-red absorption bands of CO_2 , O_3 and H_2O , respectively, three atmospheric gases that have contributed to the primary greenhouse effect.

Of course, the argument that the primary greenhouse gases have maintained our planet at a constant temperature of ca. 290 K pre-supposes that their

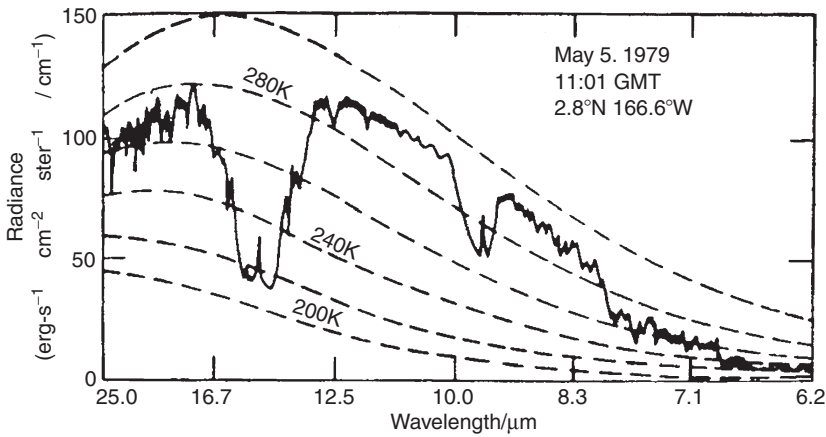


FIGURE 2 Infra-red emission spectrum escaping to space as observed by the Nimbus 4 satellite outside the earth's atmosphere. Absorptions due to CO_2 between 12 and 7 μm , O_3 (around 9.6 μm) and H_2O ($\lambda < 8 \mu\text{m}$) are shown. (With permission from Dickinson and Clark (eds.), Carbon dioxide Review, OUP, 1982.)

concentrations have remained approximately constant over very long periods of time. This has not happened with CO_2 and, to a lesser extent, with O_3 over the 260 a (years) since the start of the Industrial Revolution, ca. 1750, and it is changes in the concentrations of these and newer greenhouse gases that have caused a 'secondary' greenhouse effect to occur over this time window, leading to the temperature rises that we are all experiencing today. That, at least, is the main argument of the proponents of the 'greenhouse gases, mostly CO_2 , equals global warming' school of thought. There is no doubt that the concentration of CO_2 in our atmosphere has risen from ca. 280 parts per million by volume (ppmv) to current levels of ca. 380 ppmv over the last 260 a. (1 ppmv is equivalent to a number density of 2.46×10^{13} molecules· cm^{-3} for a pressure of 1 bar and a temperature of 298 K.) It is also not in doubt that the average temperature of our planet has risen by ca. 0.5–0.8 K over this same time window (Fig. 3). What has not been proven is that there is a cause-and-effect correlation between these two facts, the main problem being that there is not sufficient structure or resolution with time in either the CO_2 concentration or the temperature data. Even more recent data of the last 100 a (Fig. 4), where the correlation seems to be better established will not convince the sceptic. That said, as demonstrated most clearly by the recent IPCC2007 report [2], the consensus of world scientists, and certainly physical scientists, is that a strong correlation does exist.

By contrast, an excellent example in atmospheric science of sufficient resolution being present to confirm a correlation between two sets of data occurred in 1989; the concentrations of O_3 and the ClO free radical in the stratosphere were shown to have a strong anti-correlation effect when data were collected by an aircraft as a function of latitude in the Antarctic (Fig. 5) [3].

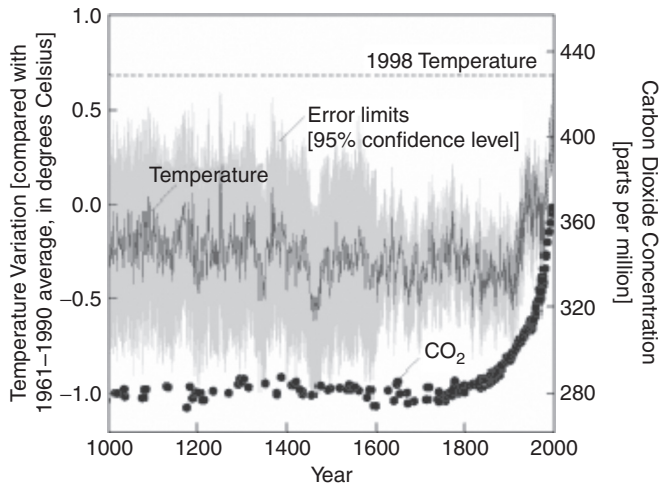


FIGURE 3 The average temperature of the earth and the concentration level of CO₂ in the earth’s atmosphere during the last 1000 a. (With permission from www.env.gov.bc.ca/air/climate/indicat/images/appendnhtemp.gif and www.env.gov.bc.ca/air/climate/indicat/images/appendCO2.gif) (See Color Plate 2).

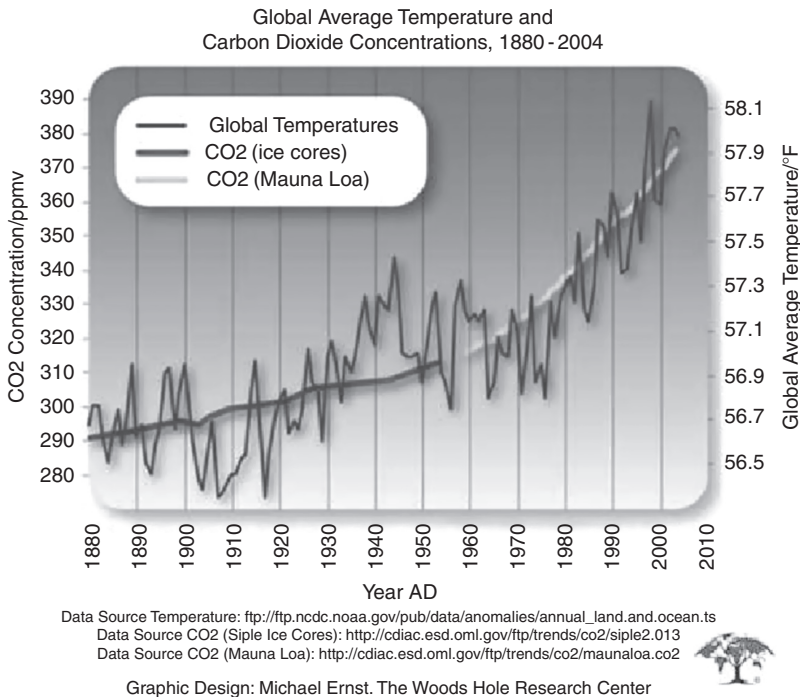


FIGURE 4 The average temperature of the earth and the concentration level of CO₂ in the earth’s atmosphere during the ‘recent’ history of the last 100 a. (With permission from the web sites shown in the figure.) (See Color Plate 3).

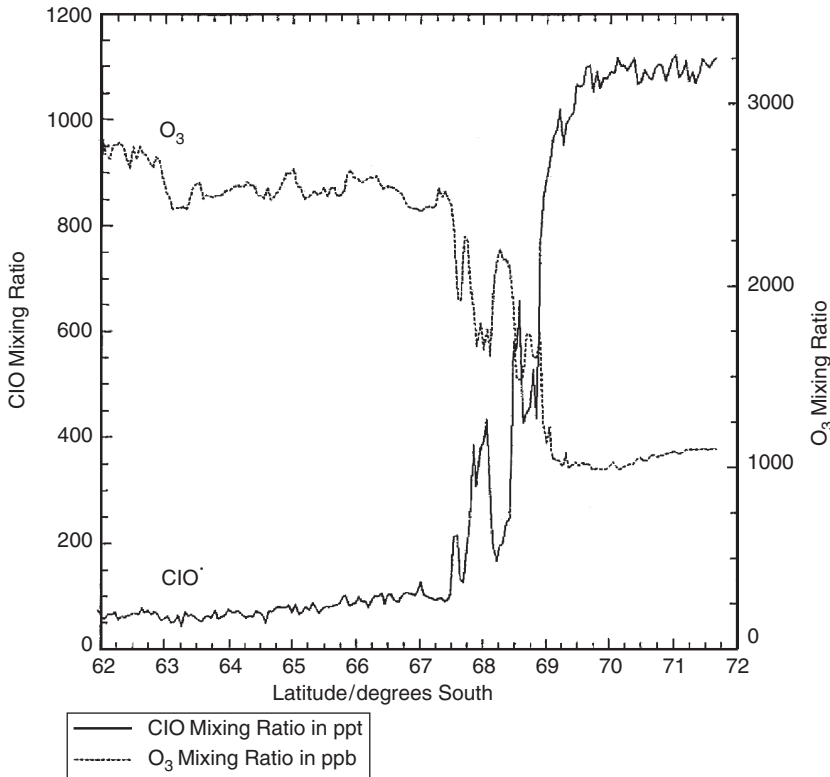


FIGURE 5 Clear anti-correlation between the concentrations of ozone, O_3 , and the chlorine monoxide radical, ClO^* , in the stratosphere above the Antarctic during their Spring season of 1987. (With permission from Anderson et al., *J. Geophys. Res. D.* 94 (1989) 11465.)

There was not only the general observation that a decrease of O_3 concentration correlated with an increase in ClO concentration, but also the resolution was sufficient to show that at certain latitudes dips in O_3 concentration corresponded exactly with rises in ClO concentration. Even the most doubting scientist could accept that the decrease in O_3 concentration in the Antarctic Spring was related somehow to the increase in ClO concentration, and this result led to an understanding over the next 10–15 a of the heterogeneous chemistry of chlorine-containing compounds on polar stratospheric clouds. Unfortunately, such good resolution is not present in the data (e.g., Figs. 3 and 4) for the ‘ CO_2 versus T ’ global warming argument, leading to the multitude of theories that are now in the public domain.

I accept that it would be very surprising if there was not some relationship between such rapid increases in CO_2 concentration and the temperature of the planet, nevertheless there are two aspects of Fig. 3 that remain unanswered by

proponents of such a simple theory. First, the data suggest that the temperature of the earth actually decreased between 1750 and ca. 1920 whilst the CO₂ concentration increased from 280 to ca. 310 ppm over this time window. Second, the drop in temperature around 1480 AD in the ‘little ice age’ is not mirrored by a similar drop in CO₂ concentration. All that said, however, the apparent ‘agreement’ between rises of both CO₂ levels and T_e over the last 50 a is very striking. The most likely explanation surely is that there are a multitude of effects, one of which is the concentrations of greenhouse gases in the atmosphere, contributing to the temperature of the planet. At certain times of history, these effects are ‘in phase’ (as now), at other times they may have been in ‘anti-phase’ and working against each other.

3. THE PHYSICAL CHEMISTRY PROPERTIES OF GREENHOUSE GASES

The fundamental physical property of a greenhouse gas is that it must absorb infra-red radiation via one or more of its vibrational modes in the infra-red range of 5–25 μm . Furthermore, since the primary greenhouse gases of CO₂, O₃ and H₂O absorb in the range 12–17 μm (or 590–830 cm^{-1}), 9.6 μm (1040 cm^{-1}) and $\lambda < 8 \mu\text{m}$ ($>1250 \text{cm}^{-1}$), an effective secondary greenhouse gas is one which absorbs infra-red radiation strongly outside these ranges of wavelengths (or wavenumbers). A molecular vibrational mode is only infra-red active if the motion of the atoms generates a dipole moment. That is, $d\mu/dQ \neq 0$, where μ is an instantaneous dipole moment and Q a displacement coordinate representing the vibration of interest. It is worth stating the obvious straightaway, that N₂ and O₂ which constitute 99% of the earth’s atmosphere do not absorb infra-red radiation, their sole vibrational mode is infra-red inactive, so they play no part in the greenhouse effect and global warming. It is only trace gases in the atmosphere (Table 1) such as CO₂ (0.038%), CH₄ (0.0002%), O₃ ($3 \times 10^{-6}\%$) and CFCs such as CF₂Cl₂ ($5 \times 10^{-8}\%$) which contribute to the greenhouse effect. Put another way, the earth’s atmosphere is particularly fragile if only 1% of the molecules present can have such a major effect on humans living on the planet. Furthermore, the most important molecular trace gas, CO₂, absorbs via its ν_2 bending vibrational mode at 667 cm^{-1} or 15.0 μm , which coincidentally is very close to the peak of the earth’s black-body curve; the spectroscopic properties of CO₂ have not been particularly kind to the environment! Thus, infra-red spectroscopy of gas-phase molecules, in particular at what wavelengths and how strongly a molecule absorbs such radiation, will clearly be important properties to determine how effective a trace pollutant will be to the greenhouse effect.

The second property of interest is the lifetime of the pollutant in the earth’s atmosphere: the longer the lifetime, the greater contribution a greenhouse gas will make to global warming. The main removal processes in the troposphere and stratosphere are reactions with OH free radicals and electronically excited

TABLE 1 Main constituents of ground-level clean air in the earth's atmosphere

Molecule	Mole fraction	ppmv ^a (2008)	ppmv (1748)
N ₂	0.78 or 78%	780 900	780 900
O ₂	0.21 or 21%	209 400	209 400
H ₂ O	0.03 (100% humidity, 298 K)	31 000	31 000
H ₂ O	0.01 (50% humidity, 298 K)	16 000	16 000
Ar	0.01 or 1%	9300	9300
CO ₂	3.8×10^{-4} or 0.038%	379	280
Ne	1.8×10^{-5} or 0.002%	18	18
CH ₄	1.77×10^{-6} or 0.0002%	1.77	0.72
N ₂ O	3.2×10^{-7} or 0.00003%	0.32	0.27
O ₃ ^b	3.4×10^{-8} or 0.000003%	0.034	0.025
All CFCs ^c	8.7×10^{-10} or $8.7 \times 10^{-8}\%$	0.0009	0
All HCFCs ^d	1.9×10^{-10} or $1.9 \times 10^{-8}\%$	0.0002	0
All PFCs ^e	8.3×10^{-11} or $8.3 \times 10^{-9}\%$	0.00008	0
All HFCs ^f	6.1×10^{-11} or $6.1 \times 10^{-9}\%$	0.00006	0

^aparts per million by volume. 1 ppmv is equivalent to a number density of 2.46×10^{13} molecules·cm⁻³ for a pressure of 1 bar and a temperature of 298 K.

^bthe concentration level of O₃ is very difficult to determine because it is poorly mixed in the troposphere. It shows large variation with both region and altitude.

^cchlorofluorocarbons (e.g., CF₂Cl₂).

^dhydrochlorofluorocarbons (e.g., CHClF₂).

^eperfluorocarbons (e.g., CF₄, C₂F₆, SF₅CF₃, SF₆).

^fhydrofluorocarbons (e.g., CH₃CF₃).

oxygen atoms, O* (¹D), and photodissociation in the range 200–300 nm (in the stratosphere) or 300–500 nm (in the troposphere). Thus, the reaction kinetics of pollutant gases with OH and O* (¹D) and their photochemical properties in the UV/visible will yield important parameters to determine their effectiveness as greenhouse gases. All these data are incorporated into a dimensionless number, the global warming potential (GWP) or greenhouse potential (GHP) of a greenhouse gas. All values are calibrated with respect to CO₂ whose GWP value is 1. A molecule with a large GWP is one with strong infra-red absorption in the windows where the primary greenhouse gases such as CO₂, etc., do not absorb, long lifetimes, and concentrations rising rapidly due to human presence on the planet. GWP values of some of the most important secondary greenhouse gases are given in the bottom row of Table 2. Note that CO₂ has the lowest GWP value of the seven greenhouse gases shown.

TABLE 2 Examples of greenhouse gases and their contribution to global warming [2,20]

Greenhouse gas	CO ₂	O ₃	CH ₄	N ₂ O	CF ₂ Cl ₂ [all CFCs]	SF ₆	SF ₅ CF ₃
Concentration (2008)/ppmv	379	0.034 ^a	1.77	0.32	0.0005 [0.0009]	5.6 × 10 ⁻⁶	1.2 × 10 ⁻⁷
ΔConcentration (1748–2008)/ppmv	99	0.009 ^a	1.05	0.05	0.0005 [0.0009]	5.6 × 10 ⁻⁶	1.2 × 10 ⁻⁷
Radiative efficiency, a ₀ /W·m ⁻² ·ppbv ⁻¹	1.68 × 10 ⁻⁵	3.33 × 10 ⁻⁵	4.59 × 10 ⁻²	3.41 × 10 ⁻⁴	0.32 [0.18–0.32]	0.52	0.60
Total radiative forcing ^b /W·m ⁻²	1.66	ca. 0.30 ^c	0.48	0.16	0.17 [0.27]	2.9 × 10 ⁻³	7.2 × 10 ⁻⁵
Contribution from long-lived greenhouse gases excluding ozone to overall greenhouse effect/% ^d	63 (57)	(10)	18 (16)	6 (5)	6 [10] (6 [9])	0.1 (0.1)	0.003 (0.003)
Lifetime, τ/a	ca. 50–200 ^f	ca. days– weeks ^g	12	120	100 [45–1700]	3200	800
Global warming potential (100 a projection)	1	– ^h	25	298	10 900 [6130–14 400]	22 800	17 700

^areference [20].

^bdue to change in concentration of long-lived greenhouse gas from the pre-Industrial era to the present time.

^can estimated positive radiative forcing of 0.35 W·m⁻² in the troposphere is partially cancelled by a negative forcing of 0.05 W·m⁻² in the stratosphere [2].

^dassumes the latest value for the total radiative forcing of 2.63 ± 0.26 W·m⁻² [2].

^eThe values in brackets show the percentage contributions when the estimated radiative forcing for ozone is included in the value for the total radiative forcing; assumes a single-exponential decay for removal of greenhouse gas from the atmosphere.

^fCO₂ does not show a single-exponential decay [4].

^gO₃ is poorly mixed in the troposphere, so a single value for the lifetime is difficult to estimate. It is removed by the reaction, OH + O₃→HO₂ + O₂. Its concentration shows large variations both with region and altitude.

^hGWP values are generally not applied to short-lived pollutants in the atmosphere, due to serious inhomogeneous changes in their concentration.

Information in the previous two paragraphs is described in qualitative and descriptive terms. However, all the data can be quantified, and a mathematical description is now presented. The term that characterises the infra-red absorption properties of a greenhouse gas is the radiative efficiency, a_o . It measures the strength of the absorption bands of the greenhouse gas, x , integrated over the infra-red black-body region of ca. $400\text{--}2000\text{ cm}^{-1}$. It is a (per molecule) microscopic property and is usually expressed in units of $\text{W}\cdot\text{m}^{-2}\cdot\text{ppbv}^{-1}$. If this value is multiplied by the change in concentration of pollutant over a defined time window, usually the 260 a from the start of the Industrial Revolution to the current day, the macroscopic radiative forcing in units of $\text{W}\cdot\text{m}^{-2}$ is obtained. (Clearly, a pollutant whose concentration has not changed over this long time window will have a macroscopic radiative forcing of zero.) One may then compare the radiative forcing of different pollutant molecules over this time window, showing the current contribution of different greenhouse gases to the total greenhouse effect. Thus, the IPCC 2007 report [2] quotes the radiative forcing for CO_2 and CH_4 in 2005 as 1.66 and $0.48\text{ W}\cdot\text{m}^{-2}$, respectively, out of a total for long-lived greenhouse gases of $2.63\text{ W}\cdot\text{m}^{-2}$. These two molecules, therefore, contribute 81% in total (63% and 18%, individually) to the global warming effect. Effectively, the radiative forcing value gives a current-day estimate of how serious a greenhouse gas is to the environment, using concentration data from the past.

The overall effect in the future of one molecule of pollutant on the earth's climate is described by its GWP (or GHP) value. It measures the radiative forcing, A_x , of a pulse emission of the greenhouse gas over a defined time period, t , usually 100 a, relative to the time-integrated radiative forcing of a pulse emission of an equal mass of CO_2 :

$$\text{GWP}_x(t) = \frac{\int_0^t A_x(t) dt}{\int_0^t A_{\text{CO}_2}(t) dt} \quad (2)$$

The GWP value therefore informs how important one molecule of pollutant x is to global warming via the greenhouse effect compared to one molecule of CO_2 , which is defined to have a GWP value of unity. It is an attempt to project into the future how serious the presence of a long-lived greenhouse gas will be in the atmosphere. (Thus, when the media state that CH_4 is 25 times as serious as CO_2 for global warming, what they are saying is that the GWP value of CH_4 , looking 100 a into the future, is 25; one molecule of CH_4 is expected to cause 25 times as much 'damage' as one molecule of CO_2 .) For most greenhouse gases, the radiative forcing following an emission at $t = 0$, takes a simple exponential form:

$$A_x(t) = A_{o,x} \exp\left(\frac{-t}{\tau_x}\right) \quad (3)$$

where τ_x is the lifetime for removal of species x from the atmosphere. For CO_2 , a single-exponential decay is not appropriate since the lifetime ranges from 50 to 200 a, and we can write:

$$A_{\text{CO}_2}(t) = A_{0,\text{CO}_2} \left[b_0 + \sum_i b_i \exp\left(\frac{-t}{\tau_i}\right) \right] \quad (4)$$

where the response function, the bracket in the right-hand side of Eq. (4), is derived from more complete carbon cycles. Values for b_i ($i = 0-4$) and τ_i ($i = 1-4$) have been given by Shine *et al.* [4]. It is important to note that the radiative forcing, A_0 , in Eqs. (2)–(4) has units of $\text{W}\cdot\text{m}^{-2}\cdot\text{kg}^{-1}$. For this reason, it is given a different symbol to the microscopic radiative efficiency, a_0 , with units of $\text{W}\cdot\text{m}^{-2}\cdot\text{ppbv}^{-1}$. Conversion between the two units is simple [4]. The time integral of the large bracket on the right-hand side of Eq. (4), defined K_{CO_2} , has dimensions of time, and takes values of 13.4 and 45.7 a for a time period of 20 and 100 a, respectively, the values of t for which GWP values are most often quoted. Within the approximation that the greenhouse gas, x , follows a single-exponential time decay in the atmosphere, it is then possible to parameterise Eq. (2) to give an exact analytical expression for the GWP of x over a time period t :

$$\frac{\text{GWP}_x(t)}{\text{GWP}_{\text{CO}_2}(t)} = \frac{\text{MW}_{\text{CO}_2}}{\text{MW}_x} \cdot \frac{a_{0,x}}{a_{0,\text{CO}_2}} \cdot \frac{\tau_x}{K_{\text{CO}_2}} \cdot \left[1 - \exp\left(\frac{-t}{\tau_x}\right) \right] \quad (5)$$

In this simple form, the GWP only incorporates values for the radiative efficiency of greenhouse gases x and CO_2 , $a_{0,x}$ and a_{0,CO_2} ; the molecular weights of x and CO_2 ; the lifetime of x in the atmosphere, τ_x ; the time period into the future over which the effect of the pollutant is determined; and the constant K_{CO_2} which can easily be determined for any value of t . Thus the GWP value scales with both the lifetime and the microscopic radiative forcing of the greenhouse gas, but it remains a microscopic property of one molecule of the pollutant. The recent rate of increase in concentration of a pollutant (e.g., the rise in concentration per annum over the last decade), one of the factors of most concern to policymakers, does not contribute directly to the GWP value. This and other factors [4] have caused criticism of the use of GWPs in policy formulation.

Data for seven greenhouse gases are shown in Table 2. CO_2 and O_3 constitute naturally occurring greenhouse gases whose concentration levels ideally would have remained constant at pre-industrial revolution levels. Although H_2O vapour is the most abundant greenhouse gas in the atmosphere, it is neither long-lived nor well mixed: concentrations range 0–3% (i.e., 0–30 000 ppmv) over the planet, and the average lifetime is only a few days. Its average global concentration has not changed significantly in the

last 260 a, and it therefore has zero radiative forcing. CH_4 and N_2O constitute naturally occurring greenhouse gases with larger a_0 values than that of CO_2 . The CH_4 concentration, although small, has increased by ca. 150% since pre-industrial times. After CO_2 , it is the second most important greenhouse gas, and its current total radiative forcing is ca. 29% that of CO_2 . N_2O concentration has increased only by ca. 16% over this same time period. It has the fourth highest total radiative forcing of all the naturally occurring greenhouse gases, following CO_2 , CH_4 and O_3 . Dichlorofluoromethane, CF_2Cl_2 , is one of the most common of CFCs. These are man-made chemicals that have grown in concentration from zero in pre-industrial times to a current total concentration of 0.9 ppbv (1 ppbv is equivalent to 1 part per 10^9 (billion) by volume, or a number density of 2.46×10^{10} molecules $\cdot\text{cm}^{-3}$ at 1 bar pressure and a temperature of 298 K). Their concentration is now decreasing due to the 1987 Montreal and later International Protocols, introduced to halt stratospheric ozone destruction and (ironically) nothing to do with global warming! SF_6 and SF_5CF_3 are two long-lived halocarbons with currently very low concentration levels, but with high annual percentage increases and exceptionally long lifetimes in the atmosphere. They have very high a_0 and GWP values, essentially because of their large number of strong infra-red-active vibrational modes and their long lifetimes.

It is noted that CO_2 and CH_4 have the lowest GWP values of all greenhouse gases. Why, then, is there such concern about levels of CO_2 in the atmosphere, and with the possible exception of CH_4 no other greenhouse gas is hardly ever mentioned in the media? The answer is that the overall contribution of a pollutant to the greenhouse effect, present and future, involves a convolution of its concentration with the GWP value. Thus CO_2 and CH_4 currently contribute most to the greenhouse effect (third bottom row of Table 2) simply due to their high change in atmospheric concentration since the Industrial Revolution; note, however, that the a_0 and GWP values of both gases are relatively low. Indeed, the ν_2 bending mode of CO_2 at 15.0 μm , which is the vibrational mode most responsible for greenhouse activity in CO_2 , is close to saturation. By contrast, SF_5CF_3 is a perfluorocarbon molecule with the highest microscopic radiative forcing of any known greenhouse gas (earning it the title ‘super’ greenhouse gas [5,6]), even higher than that of SF_6 . SF_6 is an anthropogenic chemical used extensively as a dielectric insulator in high-voltage industrial applications, and the variations of concentration levels of SF_6 and SF_5CF_3 with time in the last 50 a have tracked each other very closely [7]. The GWP of these two molecules is very high, SF_6 being slightly higher because of its atmospheric lifetime, ca. 3200 a [8], is about four times greater than that of SF_5CF_3 . However, the contribution of these two molecules to the overall greenhouse effect is still very small because their atmospheric concentrations, despite rising rapidly at the rate of ca. 6–7% per annum, are still very low, at the level of parts per 10^{12} (trillion) by volume; 1 pptv is equivalent to a number density of 2.46×10^7 molecules $\cdot\text{cm}^{-3}$ at 1 bar and 298 K).

In conclusion, the macroscopic properties of greenhouse gases, such as their method of production, their concentration and their annual rate of increase or decrease, are mainly controlled by environmental and sociological factors, such as industrial and agricultural methods, and ultimately population levels on the planet. The microscopic properties of these compounds, however, are controlled by factors that undergraduates world-wide learn about in science degree courses: infra-red spectroscopy, reaction kinetics and photochemistry. Data from such lab-based studies determine values for two of the most important parameters for determining the effectiveness of a greenhouse gas: the microscopic radiative efficiency, a_o , and the atmospheric lifetime, τ .

4. THE LIFETIME OF A GREENHOUSE GAS IN THE EARTH'S ATMOSPHERE

The microscopic radiative efficiency of a greenhouse gas is determined by measuring absolute absorption coefficients for infra-red-active vibrations in the range ca. 400–2000 cm^{-1} and integrating over this region of the electromagnetic spectrum. Its meaning is unambiguous. The lifetime, however, is a term that can mean different things to different scientists, according to their discipline. It is, therefore, pertinent to describe exactly what is meant by the lifetime of a greenhouse gas (penultimate row of Table 2), and how these values are determined.

To a physical chemist, the lifetime generally means the inverse of the pseudo-first-order rate constant of the dominant chemical or photolytic process that removes the pollutant from the atmosphere. Using CH_4 as an example, it is removed in the troposphere via oxidation by the OH free radical, $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$. The rate coefficient for this reaction at 298 K is $6.4 \times 10^{-15} \text{ cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$ [9], so the lifetime is approximately equal to $(k_{298}[\text{OH}])^{-1}$. Assuming the tropospheric OH concentration to be 0.05 pptv or $1.2 \times 10^6 \text{ molecules} \cdot \text{cm}^{-3}$ [2], the lifetime of CH_4 is calculated to be ca. 4 a. This is within a factor of three of the accepted value of 12 a (Table 2). The difference arises because CH_4 is not emitted uniformly from the earth's surface, a finite time is needed to transport CH_4 via convection and diffusion into the troposphere, and oxidation occurs at different altitudes in the troposphere where the OH concentration varies from its average value of $1.2 \times 10^6 \text{ molecules} \cdot \text{cm}^{-3}$. We can regard this as an example of a two-step kinetic process,



with first-order rate constants k_1 and k_2 . The first step, $\text{A} \rightarrow \text{B}$, represents the transport of the pollutant into the atmosphere, whilst the second step, $\text{B} \rightarrow \text{C}$, represents the chemical or photolytic process (e.g., reaction with an OH radical in the troposphere) that removes the pollutant from the atmosphere. In

general, the overall rate of the process (whose inverse is called the lifetime) will be a function of both k_1 and k_2 , but its value will be dominated by the slower of the two steps. Thus, in calculating the lifetime of CH_4 simply by determining $(k_{298}[\text{OH}])^{-1}$, we are assuming that the first step, transport into the region of the atmosphere where chemical reactions occurs, is infinitely fast compared to the removal process.

The exceptionally long-lived greenhouse gases in Tables 1 and 2 (e.g., SF_6 , CF_4 , SF_5CF_3) behave in the opposite sense. Now, the slow, rate-determining process is the first step, that is, transport of the greenhouse gas from the surface of the earth into the region of the atmosphere where chemical removal occurs. The chemical or photolytic processes that ultimately remove SF_6 , etc., will have very little influence on the lifetime, that is, $k_1 \ll k_2$ in Eq. (6). These molecules do not react with OH or O^* (^1D) to any significant extent, and are not photolysed by visible or UV radiation in the troposphere or stratosphere. They therefore rise higher into the mesosphere ($h > 60$ km) where the dominant processes that can remove pollutants are electron attachment and vacuum-UV photodissociation at the Lyman- α wavelength of 121.6 nm [6]. We can define a chemical lifetime, τ_{chemical} , for such species as:

$$\tau_{\text{chemical}} = [k_e[\text{e}^-] + \sigma_{121.6}J_{121.6}\Phi_{121.6}]^{-1} \quad (7)$$

k_e is the electron attachment rate coefficient, $\sigma_{121.6}$ is the absorption cross-section at this wavelength, $[\text{e}^-]$ is the average number density of electrons in the mesosphere, $J_{121.6}$ is the mesospheric solar flux and $\Phi_{121.6}$ the quantum yield for dissociation at 121.6 nm. Often, the photolysis term is much smaller than the electron-attachment term, and the second term of the squared bracket in Eq. (7) is ignored. It is important to appreciate that the value of τ_{chemical} is a function of position, particularly altitude, in the atmosphere. In the troposphere, τ_{chemical} will be infinite because both the concentration of electrons and $J_{121.6}$ are effectively zero, but in the mesosphere τ_{chemical} will be much less. However, multiplication of k_e for SF_6 , etc., by a typical electron density in the mesosphere, ca. 10^4 cm^{-3} [10], yields a chemical lifetime which is far too small and bears no relation to the true atmospheric lifetime, simply because most of the SF_6 , etc., does not reside in the mesosphere.

One may, therefore, ask where the quoted lifetimes for SF_6 , CF_4 and SF_5CF_3 of 3200, 50 000 and 800 a, respectively, come from [8,11]. The lifetimes of such long-lived greenhouse gas can only be obtained from globally averaged loss frequencies. The pseudo-first-order destruction rate coefficient for each region of the atmosphere is weighted according to the number of molecules of compound in that region,

$$\langle k \rangle_{\text{global}} = \frac{\sum_i k_i V_i n_i}{\sum_i V_i n_i} \quad (8)$$

where i is a region, k_i is the pseudo-first-order removal rate coefficient for region i , V_i is the volume of region i , and n_i is the number density of the greenhouse gas under study in region i . The lifetime is then the inverse of $\langle k \rangle_{\text{global}}$. The averaging process thus needs input from a 2- or 3-dimensional model of the atmosphere in order to supply values for n_i . This is essentially a meteorological, and not a chemical problem. It may explain why meteorologists and physical chemists sometimes have different interpretations of what the lifetime of a greenhouse gas actually means.

Many such studies have been made for SF₆ [8,12,13], and differences in the kinetic model (k_i) and the atmospheric distributions (n_i) from different climate or transport models account for the variety of atmospheric lifetimes that have been reported. The importance of both these factors has also been explored by Hall and Waugh [14]. Their results show that because the fraction of the total number of SF₆ molecules in the mesosphere is very small, the global atmospheric lifetime given by Eq. (8) is very much longer than the mesospheric, chemical lifetime given by Eq. (7). Thus, they quote that if the mesospheric loss frequency is $9 \times 10^{-8} \text{ s}^{-1}$, corresponding to a local lifetime of 129 d (days), then the global lifetime ranges between 1425 and 1975 a, according to which climate or transport model is used.

5. GENERAL COMMENTS ON LONG-LIVED GREENHOUSE GASES

In 1994, Ravishankara and Lovejoy wrote that the release of any long-lived species into the atmosphere should be viewed with great concern [15]. They noted that the CFCs, with relatively 'short' lifetimes of ca. 100 a, have had a disastrous effect over a relatively short period of time, ca. 30–50 a, on the ozone layer in the stratosphere that protects humans from harmful UV radiation. However, following implementation of international treaties (e.g., Montreal, 1987 [16]) it is now expected that the ozone layer will recover within 50–100 a [17]. At present, there are no known undesired chemical effects of low concentrations of perfluorocarbons such as CF₄ and SF₆ in the atmosphere. However, their rapidly increasing concentrations (ca. 7% per annum for SF₆) and their exceptionally long lifetimes (thousands, not hundreds of years) means that life on earth may not be able to adapt to any changes these gases may cause in the future. They suggested that all such long-lived molecules should be considered guilty, unless proven otherwise. If SF₆ is perceived potentially to be the major problem of this family of molecules, inert, dielectric gases with lower GWP values could be used as substitutes for SF₆ in industrial applications; ring-based perfluorocarbons, such as cyclic-C₄F₈ and cyclic-C₅F₈ are possibilities [18]. However, the simplest, possibly naïve, suggestion is that humans should not put up into the atmosphere any more pollutants than are absolutely necessary. The worldwide debate just starting, probably 50 a too late, is what constitutes 'absolutely necessary'.

6. CONCLUSION

In this chapter, I have only sought to explain the physical properties of greenhouse gases, and what are the factors that determine their effectiveness as pollutant gases that can cause global warming. I have not attempted to describe the natural or anthropogenic sources of these greenhouse gases, and why their concentrations have increased since the pre-Industrial era; this will be covered by other chapters in this book.

CO₂ and CH₄ currently contribute ca. 81% of the total radiative forcing of long-lived greenhouse gases (Table 2), but it is too simplistic to say that control of CO₂ levels will be the complete solution, as is often implied by politicians and the media. It is certainly true that concentration levels of CO₂ in the earth's atmosphere are a very serious cause for concern, and many countries are now putting in place targets and policies to reduce them. It is my personal belief that CO₂ levels in the atmosphere correlate strongly with lifestyle of many of the population, and with serious effort, especially in the developed world, huge reductions are possible. The challenge will be to effect policies to reduce significantly the concentration of CO₂ without seriously decreasing the standard of living of the population and negating all the benefits that technology has brought us in the last 50–100 a. I give two examples for possible policy change. First, I query whether the huge expansion in air travel within any one country at the expense of slower methods of transports (e.g., trains) is really worth all the social and economic benefits that are claimed. The price to be paid, of course, is hugely enhanced CO₂ emissions. Second, I query whether the benefits of 24 h shopping 7 days a week are really worth the extra CO₂ emissions that result from keeping shops open continuously. Would our standard of living drop significantly if shops opened for much fewer hours? Most of Switzerland closes at 4.00 p.m. on a Saturday for the rest of the weekend, yet this country is very close to the top of all international league tables for wealth creation, standard of living and levels of well-being/happiness.

CH₄ levels, however, in my opinion pose just as serious a threat to our planet as CO₂ simply because they will be much harder to reduce. Whilst it is surprising and remains unclear why the total radiative forcing of methane, 0.48 W·m⁻², has remained unchanged over the last decade [2], a major component of methane emissions correlates strongly with the number of animal livestock which itself is dependent on the population of the planet. Controlling, let alone reducing world-wide population levels over the short period of time that is apparently available to 'save the planet' (ca. 20–40 a) [19] is a major task. Surely, this could and should be the major policy directive of the United Nations over the next few decades.

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