# The Role of Atmospheric Gases in Global Warming

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*Chapter 1*   **(final 3.11.08)**
# 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 fourteen years ago that the newly-appointed Secretary of State for the Environment in the UK 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, 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 *vs.* wavelength for a black body was worked out by Planck in the first part of the 20$^{th}$ 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 $(T/K)^4$. Second, the wavelength of the maximum in the emission distribution curve varies inversely with $(T/K)$, *i.e.* $\lambda_{max} \propto (T/K)^{-1}$. These are Stefan's and Wien's 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 $T_{sun} = 5780\ K$. The temperature of the earth is a factor of twenty lower, so the earth's black-body emission curve peaks at a wavelength which is twenty 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 J·s$^{-1}$·m$^{-2}$), $R_e$ is the radius of the Earth (6.38 x 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 infrared 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 x 10$^{-8}$ J·s$^{-1}$·m$^{-2}$·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 :

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

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 $^o$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 infrared 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 of 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 infrared radiation in the atmosphere comes from satellite data. Fig. 2 shows data collected by the Nimbus 4 satellite circum-navigating the earth at an altitude outside the earth's troposphere ($0 <$ altitude, $h < 10$ km) and stratosphere ($10 < h < 50$ km). The infrared 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 12–17 μm, around 9.6 μm, and $\lambda < 8$ μm. These wavelengths correspond to infrared 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 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 $2.46 \times 10^{13}$ 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 years (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]. 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 '$CO_2$ *vs. 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 suggests that the temperature of the earth actually decreased between 1750 and *ca.* 1920 whilst the $CO_2$ 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 $CO_2$ concentration. All that said, however, the apparent 'agreement' between rises of both $CO_2$ 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 have been '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 infrared radiation *via* one or more of its vibrational modes in the infrared range of 5–25 μm. Furthermore, since the primary greenhouse gases of $CO_2$, $O_3$ and $H_2O$ absorb in the range 12–17 μm (or 590–830 cm$^{-1}$), 9.6 μm (1040 cm$^{-1}$) and $\lambda < 8$ μm (> 1250 cm$^{-1}$), an effective secondary greenhouse gas is one which absorbs inrared radiation strongly *outside* these ranges of wavelengths (or wavenumbers). A molecular vibrational mode is only infrared active if the motion of the atoms generates a dipole moment. That is, $d\mu/dQ \neq 0$, where $\mu$ is an instantaneous dipole moment and $Q$ a displacement coordinate representing the vibration of interest. It is worth stating the obvious straightaway, that $N_2$ and $O_2$ which constitute 99 % of the earth's atmosphere do not absorb infrared radiation, their sole vibrational mode is infrared 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 $CO_2$ (0.038 %), $CH_4$ (0.0002 %), $O_3$ (3 x 10$^{-6}$ %) and chlorofluorocarbons such as $CF_2Cl_2$ (5 x 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, $CO_2$, absorbs *via* its $\nu_2$ 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 $CO_2$ have not been particularly kind to the environment! Thus, infrared 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 oxygen atoms, O* ($^1$D), 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* ($^1$D) 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 $CO_2$ whose GWP value is 1. A molecule with a large GWP is one with strong infrared absorption in the windows where the primary greenhouse gases such as $CO_2$ *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 $CO_2$ has the lowest GWP value of the seven greenhouse gases shown.

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 infrared 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 infrared black-body region of *ca.* 400–2000 cm$^{-1}$. It is a (per molecule) microscopic property and is usually expressed in units of W·m$^{-2}$·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 W·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 W·m$^{-2}$, respectively, out of a total for long-lived greenhouse gases of 2.63 W·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 $CO_2$ :

$$\text{GWP}_x(t) \; = \; \frac{\int_0^t A_x(t).dt}{\int_0^t A_{CO2}(t).dt} \tag{2}$$

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 :

$$A_x(t) \; = \; A_{o,x} \exp(-t \, / \, \tau_x) \tag{3}$$

where $\tau_x$ 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 :

$$A_{CO2}(t) \; = \; A_{o,CO2} \left[ b_o + \sum_i b_i \exp(-t \, / \, \tau_i) \right] \tag{4}$$

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 $\tau_i$ ($i = 1$–4) have been given by Shine *et al.* [4]. It is important to note that the radiative forcing, $A_o$, in Eqs. (2)–(4) has units of $W \cdot m^{-2} \cdot kg^{-1}$. For this reason, it is given a different symbol to the microscopic radiative efficiency, $a_o$, with units of $W \cdot m^{-2} \cdot ppbv^{-1}$. Conversion between the two units is simple [4]. The time integral of the large bracket on the right-hand side of Eq. (4), defined $K_{CO2}$, 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 $t$ :

$$\frac{GWP_x(t)}{GWP_{CO2}(t)} = \frac{MW_{CO2}}{MW_x} \cdot \frac{a_{o,x}}{a_{o,CO2}} \cdot \frac{\tau_x}{K_{CO2}} \cdot \left[ 1 - \exp\left(\frac{-t}{\tau_x}\right) \right] \tag{5}$$

In this simple form, the GWP only incorporates values for the radiative efficiency of greenhouse gases $x$ and $CO_2$, $a_{o,x}$ and $a_{o,CO2}$ ; the molecular weights of $x$ and $CO_2$ ; the lifetime of $x$ in the atmosphere, $\tau_x$ ; the time period into the future over which the effect of the pollutant is determined ; and the constant $K_{CO2}$ 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 from 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 $a_o$ 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 chlorofluorocarbons. 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 x $10^{10}$ molecules·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 $a_o$ and GWP values, essentially because of their large number of strong infrared-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 $a_o$ and GWP values of both gases are relatively low. Indeed, the $\nu_2$

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 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 x $10^7$ molecules·$cm^{-3}$ 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 : infrared 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 infrared-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, OH + $CH_4 \rightarrow H_2O + CH_3$. The rate coefficient for this reaction at 298 *K* is 6.4 x $10^{-15}$ $cm^3$·molecule$^{-1}$·$s^{-1}$ [9], so the lifetime is approximately equal to $(k_{298}[OH])^{-1}$. Assuming the tropospheric OH concentration to be 0.05 pptv or 1.2 x $10^6$ molecules·$cm^{-3}$ [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

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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 $1.2 \times 10^6$ molecules·cm$^{-3}$. We can regard this as an example of a two-step kinetic process,

$$A \rightarrow B \rightarrow C \tag{6}$$

with first-order rate constants $k_1$ and $k_2$. The first step, $A \rightarrow B$, represents the transport of the pollutant into the atmosphere, whilst the second step, $B \rightarrow C$, 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 $(k_{298}[OH])^{-1}$, 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, *i.e.* 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, *i.e.* $k_1 \ll k_2$ in Eq. (6). These molecules do not react with OH or O* ($^1$D) 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-$\alpha$ wavelength of 121.6 nm [6]. We can define a chemical lifetime, $\tau_{chemical}$, for such species as :

$$\tau_{chemical} = \left[ k_e[e^-] + \sigma_{121.6} J_{121.6} \Phi_{121.6} \right]^{-1} \tag{7}$$

$k_e$ is the electron attachment rate coefficient, $\sigma_{121.6}$ is the absorption cross-section at this wavelength, $[e^-]$ 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 $\tau_{chemical}$ is a function of position, particularly altitude, in the atmosphere. In the troposphere, $\tau_{chemical}$ will be infinite because both the concentration of electrons and $J_{121.6}$ are effectively zero, but in the mesosphere $\tau_{chemical}$ 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, 50000 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 psuedo-first-order destruction rate coefficient for each region of the atmosphere is weighted according to the number of molecules of compound in that region,

$$<k>_{global} = \frac{\sum_i k_i V_i n_i}{\sum_i V_i n_i} \qquad (8)$$

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 $<k>_{global}$. 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 meterological, and not a chemical problem. It may explain why meterologists and physical chemists sometimes have different interpretations of what the lifetime of a greenhouse gas actually means.

Many such studies have been made for $SF_6$ [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 $SF_6$ 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 $9 \times 10^{-8}$ $s^{-1}$, 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 that the release of any long-lived species into the atmosphere should be viewed with great concern [15]. They noted that the chlorofluorocarbons (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) it is now expected that the ozone layer will recover within 50–100 a [16]. At present, there are no known undesired chemical

effects of low concentrations of perfluorocarbons such as $CF_4$ and $SF_6$ in the atmosphere. However, their rapidly-increasing concentrations (*ca.* 7 % per annum for $SF_6$) 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 $SF_6$ 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 $SF_6$ in industrial applications ; ring-based perfluorocarbons, such as *cyclic*-$C_4F_8$ and *cyclic*-$C_5F_8$ are possibilities [17]. 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.

$CO_2$ and $CH_4$ 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 $CO_2$ levels will be the complete solution, as is often implied by politicians and the media. It is certainly true that concentration levels of $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ emissions. Second, I query whether the benefits of 24 hour shopping 7 days a week are really worth the extra $CO_2$ 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 pm 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.

CH$_4$ levels, however, in my opinion pose just as serious a threat to our planet as CO$_2$ 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 lifestock 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) [18] 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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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 |
| $H_2O$ | 0.03 (100% humidity, 298 $K$) | 30 000 | 31 000 |
| $H_2O$ | 0.01 (50% humidity, 298 $K$) | 10 000 | 16 000 |
| Ar | 0.01 or 1 % | 9 300 | 9 300 |
| $CO_2$ | $3.8 \times 10^{-4}$ or 0.038 % | 379 | 280 |
| Ne | $1.8 \times 10^{-5}$ or 0.002 % | 18 | 18 |
| $CH_4$ | $1.77 \times 10^{-6}$ or 0.0002 % | 1.77 | 0.72 |
| $N_2O$ | $3.2 \times 10^{-7}$ or 0.00003 % | 0.32 | 0.27 |
| $O_3$ [b] | $3.4 \times 10^{-8}$ or 0.000003 % | 0.034 | 0.025 |
| All CFCs [c] | $8.7 \times 10^{-10}$ or $8.7 \times 10^{-8}$ % | 0.0009 | 0 |
| All HCFCs [d] | $1.9 \times 10^{-10}$ or $1.9 \times 10^{-8}$ % | 0.0002 | 0 |
| All PFCs [e] | $8.3 \times 10^{-11}$ or $8.3 \times 10^{-9}$ % | 0.00008 | 0 |
| All HFCs [f] | $6.1 \times 10^{-11}$ or $6.1 \times 10^{-9}$ % | 0.00006 | 0 |

[a]  parts per million by volume.  1 ppmv is equivalent to a number density of $2.46 \times 10^{13}$ molecules·cm$^{-3}$ for a pressure of 1 bar and a temperature of 298 $K$.

[b]  The concentration level of $O_3$ is very difficult to determine because it is poorly mixed in the troposphere.  It shows large variation with both region and altitude.

[c]  chlorofluorocarbons (*e.g.* $CF_2Cl_2$)

[d]  hydrochlorofluorocarbons (*e.g.* $CHClF_2$)

[e]  perfluorocarbons (*e.g.* $CF_4$, $C_2F_6$, $SF_5CF_3$, $SF_6$)

[f]  hydrofluorocarbons (*e.g.* $CH_3CF_3$)

Table 2.
Examples of greenhouse gases, and their contribution to global warming [2,19].

| 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 x 10$^{-6}$ | 1.2 x 10$^{-7}$ |
| ΔConcentration (1748–2008) / ppmv | 99 | 0.009 [a] | 1.05 | 0.05 | 0.0005 [0.0009] | 5.6 x 10$^{-6}$ | 1.2 x 10$^{-7}$ |
| Radiative efficiency, $a_o$ / W·m$^{-2}$·ppbv$^{-1}$ | 1.68 x 10$^{-5}$ | 3.33 x 10$^{-2}$ | 4.59 x 10$^{-4}$ | 3.41 x 10$^{-3}$ | 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 x 10$^{-3}$ | 7.2 x 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, $\tau$ [e] / 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 | 10900 [6130–14400] | 22800 | 17700 |

[a]   Reference [19].
[b]   Due to change in concentration of long-lived greenhouse gas from the pre-Industrial era to the present time.
[c]   An 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].
[d]   Assumes the latest value for the total radiative forcing of 2.63 ± 0.26 W·m$^{-2}$ [2].
      The values in brackets show the percentage contributions when the estimate radiative forcing for ozone
      is included in the value for the total radiative forcing.
[e]   Assumes a single-exponential decay for removal of greenhouse gas from the atmosphere.
[f]   CO$_2$ does not show a single-exponential decay [4].
[g]   O$_3$ is poorly mixed in the troposphere, so a single value for the lifetime is difficult to estimate.  It is removed by the reaction
      OH + O$_3$ → HO$_2$ + O$_2$.  Its concentration shows large variations both with region and altitude.
[h]   GWP values are generally not applied to short-lived pollutants in the atmosphere, due to serious inhomogeneous changes in
      their concentration.

*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 $\lambda_{max}\ \alpha\ (1/T)$.  The two graphs are not to scale.

*Figure 2* :  Infrared emission spectrum escaping to space as observed by the Nimbus 4 satellite outside the earth's atmosphere.  Absorptions due to $CO_2$ between $12\text{–}17\ \mu m$, $O_3$ (around 9.6 µm) and $H_2O$ ($\lambda < 8$ µm)  are shown.  (*With permission from R.E. Dickinson and W.C. Clark (eds), Carbon dioxide review (1982) OUP.)*

*Figure 3* :  The average temperature of the earth and the concentration level of $CO_2$ in the earth's atmosphere during the last 1000 years.  (*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)

*Figure 4* :  The average temperature of the earth and the concentration level of $CO_2$ in the earth's atmosphere during the 'recent' history of the last 100 years.  (*With permission from the web sites shown in the figure.*)

*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., (1989)* **94,** *11465* )
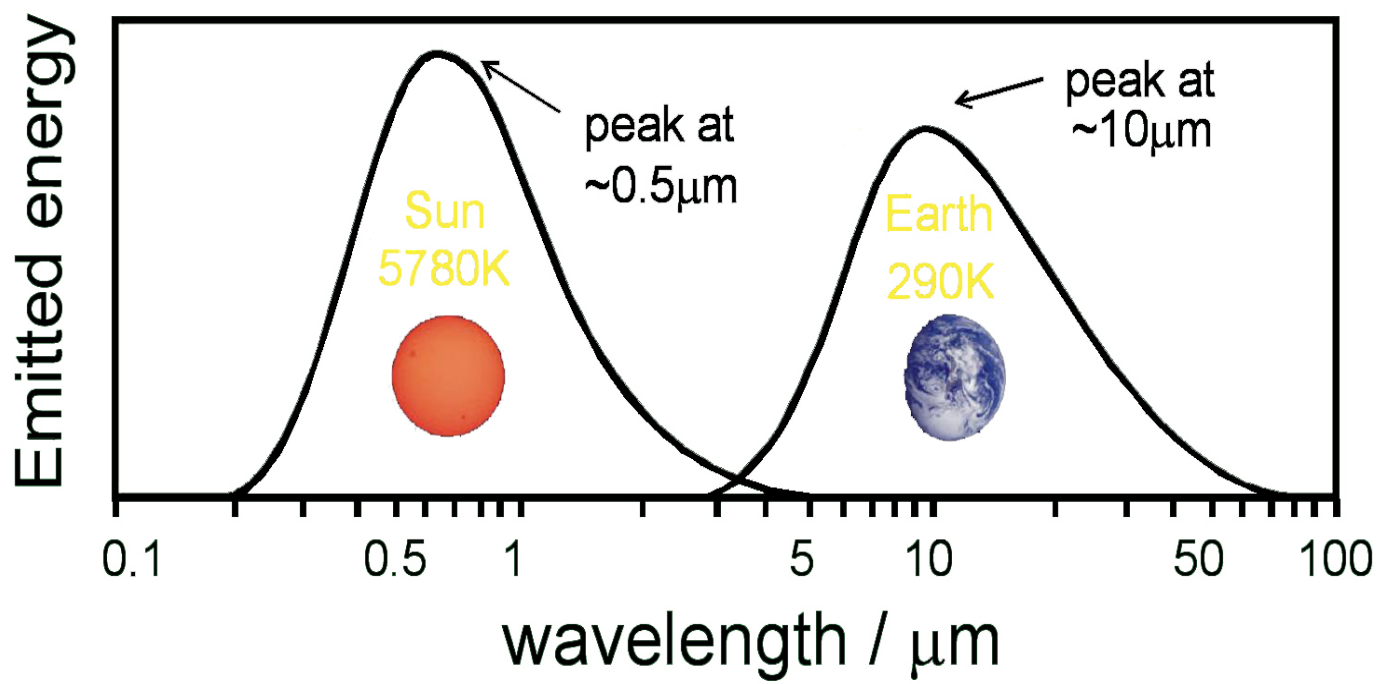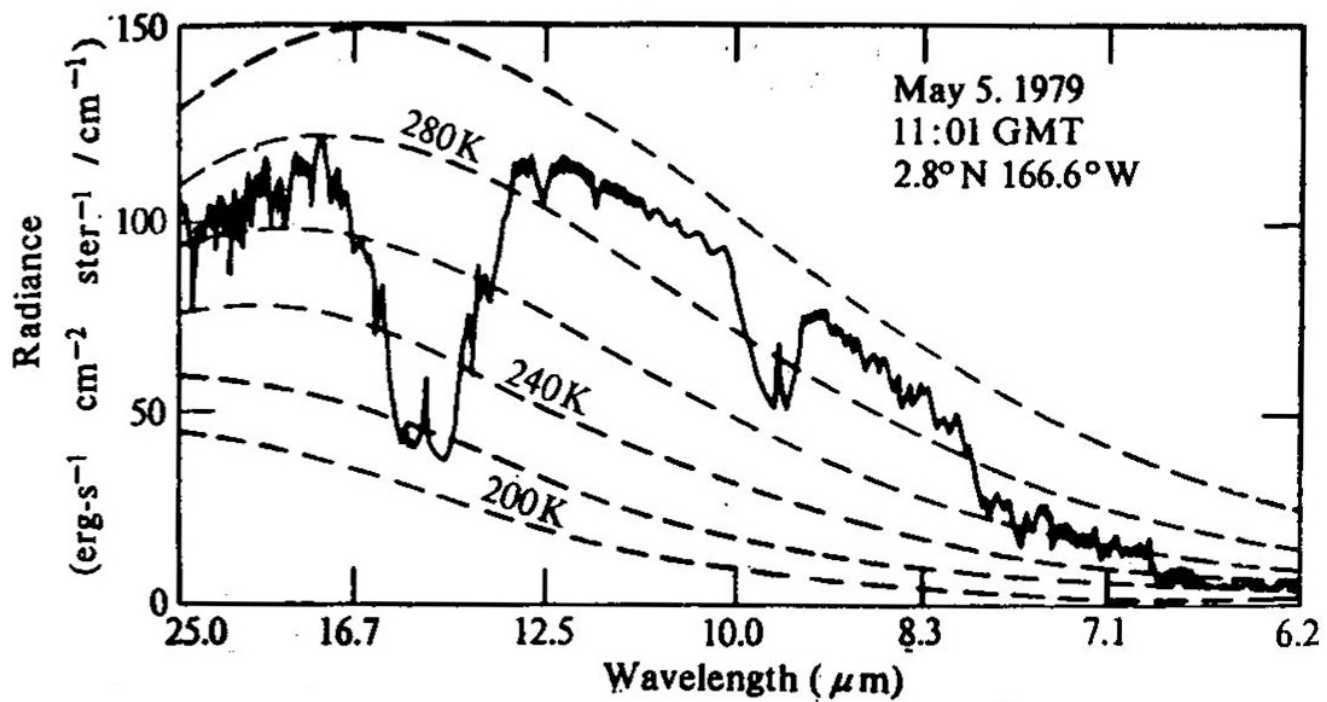
*Figure 1* :

*Figure 2* :

Figure 3 :



Temperature Variation (compared with 1961–1990 average, in degrees Celsius)

1.0
0.5
0.0
−0.5
−1.0

1998 Temperature

Error limits (95% confidence level)

Temperature

CO₂

Carbon Dioxide Concentration (parts per million)
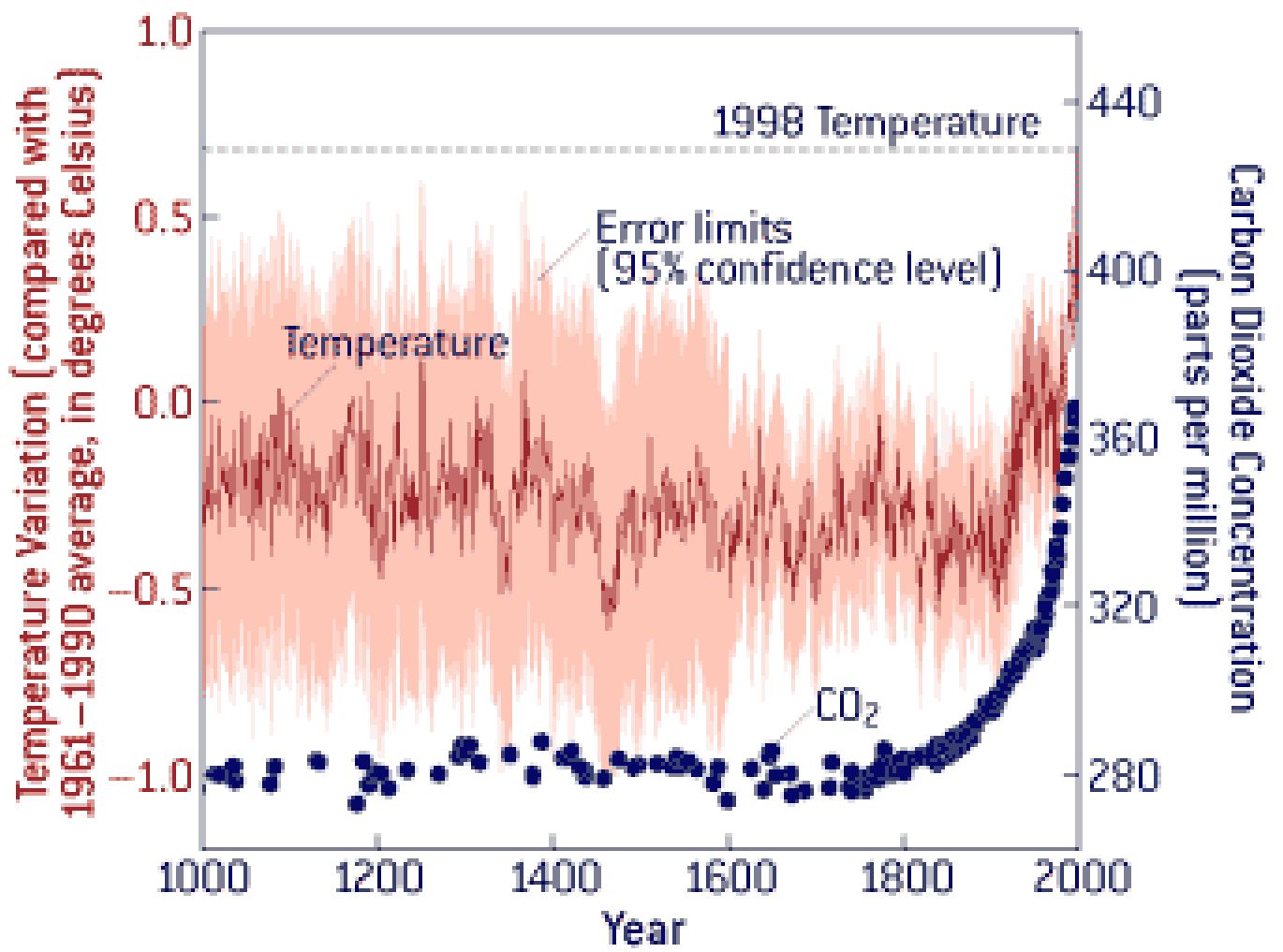
440
400
360
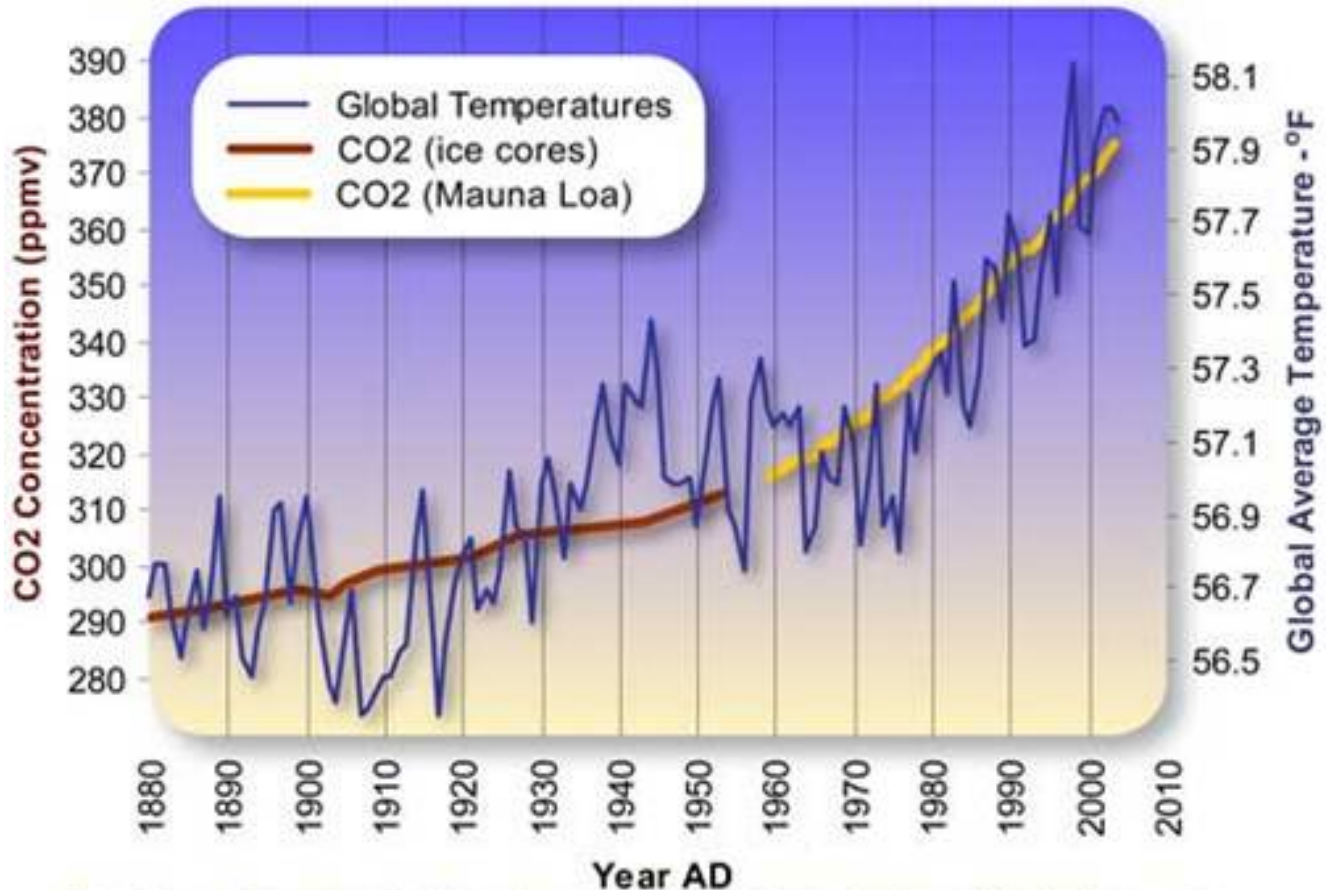320
280

1000   1200   1400   1600   1800   2000

Year

*Figure 4* :



Global Average Temperature and Carbon Dioxide Concentrations, 1880 - 2004

Data Source Temperature: ftp://ftp.ncdc.noaa.gov/pub/data/anomalies/annual_land.and.ocean.ts
Data Source CO2 (Siple Ice Cores): http://cdiac.esd.ornl.gov/ftp/trends/co2/siple2.013
Data Source CO2 (Mauna Loa): http://cdiac.esd.ornl.gov/ftp/trends/co2/maunaloa.co2

Graphic Design: Michael Ernst, The Woods Hole Research Center

*Figure 5* :