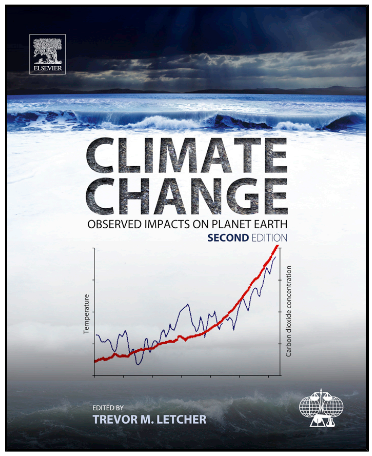

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CHAPTER

THE ROLE OF ATMOSPHERIC GASES

24

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CHAPTER OUTLINE

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1. INTRODUCTION

I wrote the opening chapter for the first edition of *Climate Change: Observed Impacts on Planet Earth in 2008* about the role of atmospheric gases in global warming [1]. My opening sentence stated that *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*. Although the science was relatively mature, it seemed to me then that it was not possible to prove, in an absolute and scientific sense, any correlation between CO_2 global concentrations and average global temperatures, with the net result that mixed messages were being portrayed to the general public. Perhaps I was being too honest because, whilst there are some inconsistencies in the data, my belief was and remains that the rise in global temperature of the planet is genuine and that humankind is the predominant cause through contributing to enhanced concentrations of carbon dioxide by the burning of excess fossil fuels. Furthermore, the public did not then, and still does not understand the concept of error or uncertainty, and any chink in the scientific data was leapt upon by climate sceptics with the voracity of a hungry animal in the wild. However, I also made the point that people should not become obsessed with CO_2 concentrations because there are other gaseous components in the Earth's atmosphere, especially CH_4, which have the capacity to cause as much damage to the environment as CO_2; Shine has made this same point consistently in the literature [2]. I highlighted also the possible future problem of gaseous compounds that have exceptionally long lifetimes in the atmosphere, many hundreds if not thousands of years; perfluorinated compounds, such as CF_4, SF_6,

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CF_3SF_5 and NF_3, fall into this category. Whilst their concentrations currently might be fairly small, they have the capacity to cause serious problems if their concentrations are allowed to increase in an unchecked manner.

In this second edition of *Climate Change*, I update the chapter, but with enhanced experience of leading talks and discussions on this topic to many schools, colleges, universities and voluntary organizations of intelligent lay people over the last 10 years. I pose throughout three slightly different questions to what I wrote about in 2008. First: has the basic science and knowledge base changed in the last six years? Second: have public perceptions about possible global warming and climate change changed, and if so, in what direction? Third: assuming that there is a global problem brewing in the near future, have direct actions or policies been or are being developed to counter the perceived threat? I conclude the chapter with what I perceive as some simple-to-implement, some difficult-to-implement and some incredibly complex issues that must be addressed by us all if this huge threat to civilization, as we know it on this planet, is to be controlled.

2. MYTHS, FACTS, LIES AND OPINIONS ABOUT THE GREENHOUSE EFFECT

I have come to the conclusion that there are several myths that have grown into the conscience of many of the general public on this subject. Like all myths, they need to be corrected as quickly as possible. The first is that the greenhouse effect is all ‘bad news’. As I show in Section 3, nothing could be further from the truth, and without the greenhouse effect the average temperature of our planet would be that of winter in Siberia, i.e. down to $-17°C$ (256 K). Secondly, the greenhouse and ozone depletion, if not quite the same effect, have similar scientific explanations and causes. Whilst understandable up to a point because some chemicals, such as gaseous chlorofluorocarbon molecules, contribute to both effects, the basic science of the two effects is very different; furthermore, the former is a property of the troposphere (altitude $h = 0$ km–15 km) whilst the latter is a property of the stratosphere ($h = 15$ km–50 km). Thirdly, and perhaps the most serious issue, is that the large majority of the world’s population regard *weather* and *climate* as the same phenomenon. This is not true. The former is a short-term phenomenon on which we base our daily actions; at its simplest and most banal, what is the weather forecast for tomorrow, so what clothes do we wear? The latter is a very long-term phenomenon, taking data from the past to model patterns for the future, the timescales being tens to hundreds of years in both cases. So it is nonsense to say, for example, that just because the winter of 2012–2013 in the UK was very cold, there is no problem ahead. Yet I hear this sort of prejudice from friends and neighbours with disturbing regularity.

What facts are indisputable? In decreasing order of certainty, first, I believe nobody can argue with the observation, made at many observation points around the world (e.g. Fig. 1), that average CO_2 concentrations are increasing slowly, year on year, and the value for 2014 was 400 parts per million by volume (ppmv; or 400 μmol mol^{-1}), the highest ever recorded; the value in preindustrial Britain was *ca.* 280 ppmv. Furthermore, the concentrations of other long-lived greenhouse gases such as CH_4 and N_2O are also increasing year on year, as reported on an annual basis since 2006 with great accuracy by the World Meteorological Organization Greenhouse Gas Bulletins [3]. Secondly, I believe the evidence is strong that average global temperatures are also rising; they have risen somewhere between 0.6°C and 1.0°C since the preindustrial era, but the certainty level in this statement is lower simply because of the greater uncertainty in the data. Thirdly, the region of the

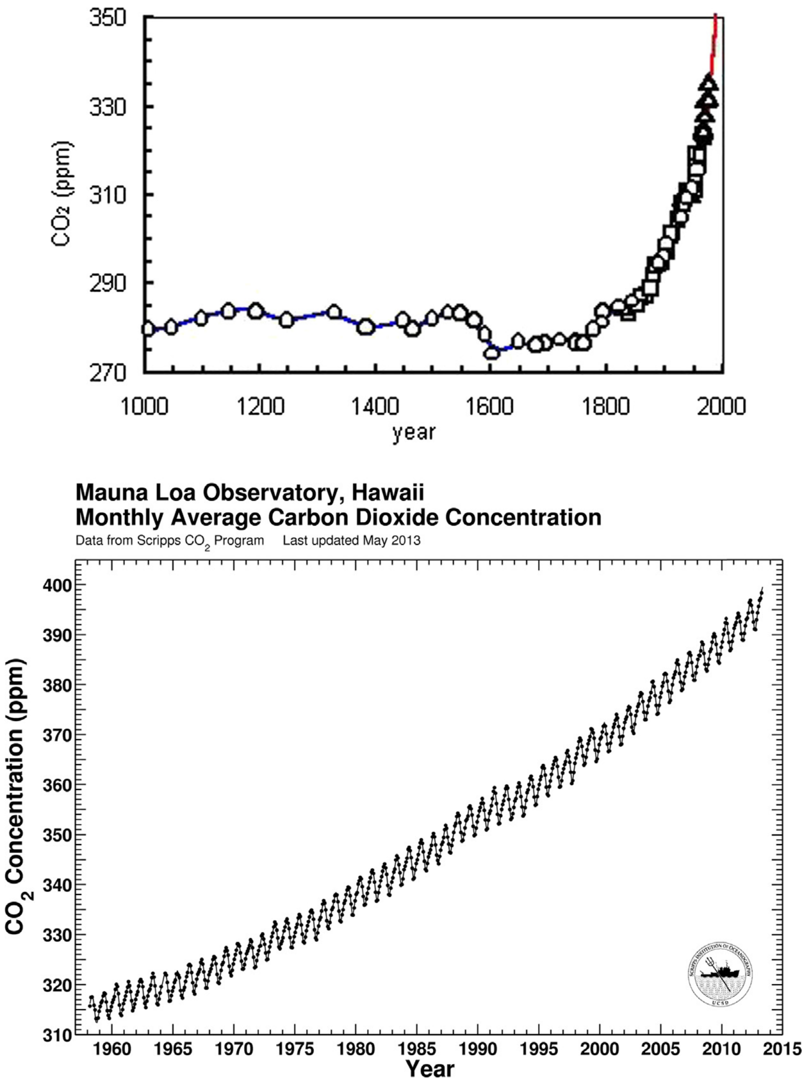

FIGURE 1

The increasing levels of CO_2 in the Earth's atmosphere. The upper picture comes from www.ems.psu.edu (with permission), showing the approximate constant concentration of CO_2 from AD 1000 to *ca.* AD 1750, the start of the Industrial Revolution, of about 280 μmol mol^{-1} (or 280 ppmv); there is a slow but consistent rise thereafter. The lower picture shows data for the last 55 years, recorded at the Mauna Loa Observatory in Hawaii, highlighting the relentless increase in concentration year by year. *(With permission from www.esrl.noaa.gov.)* The small oscillations every six months are caused by seasonal changes due to photosynthetic activity of vegetation, which consumes CO_2; the extent of the oscillation is reduced when the data are recorded in regions, such as Antarctica, with smaller amounts of vegetation. Note: the *y*-axis label should read: CO_2 concentration/μmol mol^{-1}.

Earth's atmosphere where global warming occurs is the troposphere, the first 15 km of altitude above the Earth's surface. Yet this is the region of the atmosphere where both homogeneous and heterogeneous processes take place, including reactions on aerosol surfaces, and I believe that the chemistry of this region is the least well understood. Fourthly, whilst the large majority of scientists in the world do believe that there is a correlation between the increasing CO_2 concentration and the very probable rise in the Earth's temperature, from a mathematical point of view it is difficult to *prove* the correlation because there is simply not the signal-to-noise ratio and/or resolution in the data. I discuss this point further in Section 3.

What are opinions and what are downright untruths in this increasingly political subject? It is rumoured that George Bush infamously said during his eight-year US presidency at the start of the twenty-first century words to the effect that *Global warming is not occurring. Even if it is, it is unrelated to man's activities on earth*. He might have added, *and certainly not us in the USA*! More comically, he was once quoted as saying, *I have opinions of my own, strong opinions, but I don't always agree with them*. Whilst this second quote is amusing and harmless, the first is verging on an untruth because nearly all the scientific evidence from the first decade of the twenty-first century does not support this statement. Yet, such opinions, coming from one of the most powerful and influential people in the world, can be dangerous if they turn out to be untrue because millions of North Americans will take their lead from the president of the day. In this way, prejudices are born. Conversely, on this side of the Atlantic Ocean, Professor David King, the chief scientific advisor to the UK Government, was making statements at the same time to the effect that *Global warming is the most serious phenomenon affecting the world's security and prosperity, more so than terrorism* [4]. King has since claimed he was misquoted and the statement was taken out of context, but the fact remains that, whoever said what or meant what, the US and the UK were taking diametrically opposite positions on this major area of public policy. Such divergence between two countries normally joined at the hip has been very rare in the last 50 years. The two countries are now led by Barack Obama and David Cameron, and they are exploring much more similar areas of policy for controlling greenhouse emissions. This must be welcomed.

What do scientists think? The huge majority working in different disciplines now do believe that the correlation between CO_2 concentrations and the temperature of the planet is as good as proven, and the temperature of the planet will rise from pre-Industrial levels anywhere between 2 K and 5 K by the end of the twenty-first century; the lower end of this range if CO_2 emissions can be stabilized then reduced, the higher end if no controls are put in place. The language of the Fifth Assessment Report of the United Nations Intergovernmental Panel on Climate Change (IPCC) from 2013 is that much stronger than that of the preceding report of 2007 [5,6], and I believe these huge documents have the support of at least 99% of the world's scientists. This was probably not the case for the earlier UN reports in the late twentieth century. A very small minority of scientists believe that, whilst the temperature of the planet may be increasing, this global warming is *not* due to humankind's activities since the Industrial Revolution but to a natural cycle of ice ages with warm periods in between; in other words, we are currently in a warm period between ice ages, and coincidentally this is happening at the same time as the global CO_2 concentration is increasing. This has been refuted by world experts – see Chapter 25. An even smaller number of people, who tend to be loud and articulate nonscientists, deny the existence of global warming and climate change at all. In a democracy everyone is entitled to their opinions, but in time I am convinced such people will be seen as the ultimate 'flat earthers' who will deny whatever evidence is presented to them.

3. ORIGIN OF THE GREENHOUSE EFFECT: 'PRIMARY' AND 'SECONDARY' EFFECTS

Much of this section is unchanged from the first edition because I contend that the basic science of the greenhouse effect has not changed. All that has changed are improvements in data relating to individual gases that contribute to the overall (secondary) greenhouse effect, and some new greenhouse gases have been discovered in the atmosphere since 2008.

The different regions of the Earth's atmosphere are shown in Fig. 2. The total gas pressure in the atmosphere decreases exponentially with altitude, h. We can write that $p_h = p_0\exp(-h/h_0)$, with the scale height, h_0, having a value of *ca.* 8500 m or 8.5 km. The temperature drops at a uniform rate through the troposphere ($0 < h <$ *ca.* 10 km) from *ca.* 298 K to 210 K, and visible photochemistry (wavelength, $\lambda >$ *ca.* 390 nm) dominates in this region. A temperature inversion occurs over the next 40 km of altitude through the stratosphere (*ca.* $10 < h <$ *ca.* 50 km), but the total gas pressure keeps dropping at an exponential rate. The temperature inversion leads to a very stable gas-phase environment, ozone depletion takes place in this region of the atmosphere, and ultraviolet (UV) photochemistry ($200 < \lambda <$ *ca.* 390 nm) dominates. The mesosphere and ionosphere lie above the stratosphere, where reactions of charged particles such as cations, anions and free electrons can be important; vacuum-UV photochemistry ($\lambda <$ *ca.* 200 nm), especially at the Lyman-α wavelength of 121.6 nm, can also be an important process in these two regions. The Earth is a planet in dynamic

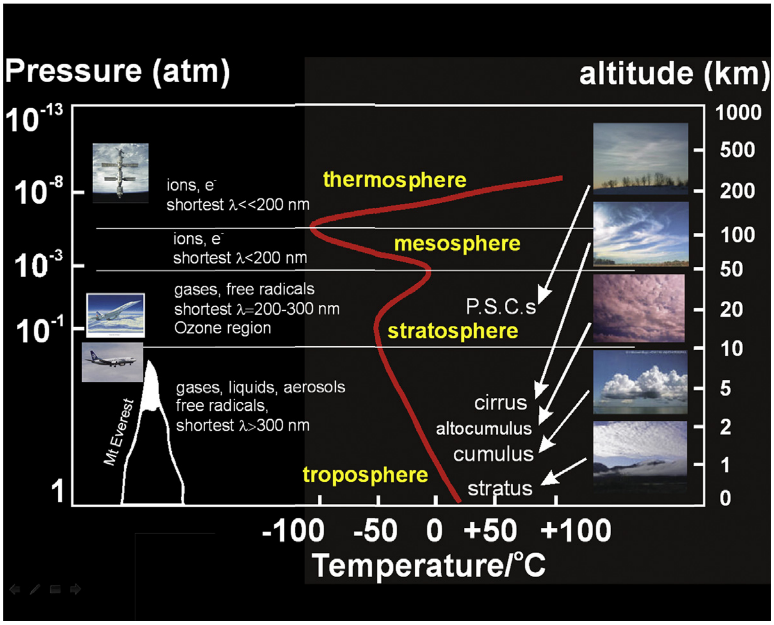

FIGURE 2

Different regions of the Earth's atmosphere. About 90% of the gases exist in the troposphere, of which *ca.* 99% are either N_2 or O_2. Visible photochemistry dominates in the troposphere ($\lambda >$ *ca.* 390 nm), UV in the stratosphere ($200 < \lambda <$ *ca.* 390 nm), and vacuum-UV in the mesosphere and thermosphere/ionosphere ($\lambda < 200$ nm). Note that 1 atm of pressure is equivalent to 101 325 Pa. The left-hand *y*-axis label should read: Pressure/atm and the right-hand *y*-axis label should read Altitude/km.

equilibrium since it continually absorbs and emits electromagnetic radiation. As described above, it receives or absorbs vacuum-UV, UV and visible radiation from the sun, and photochemistry of gaseous molecules can occur in different regions of the atmosphere. To maintain energy balance and a constant temperature the Earth must emit electromagnetic radiation, which it does in the form of infrared radiation. By energy balance, 'energy in' must equal 'energy out', and this equality determines what the average temperature of the planet should be.

Both the sun and planet Earth are black body emitters of electromagnetic radiation. That is, they are bodies capable of emitting and absorbing all frequencies (or wavelengths) of electromagnetic radiation uniformly according to the laws of quantum physics. The distribution curve of emitted energy per unit time per unit area versus wavelength for a black body was determined by Planck in the first part of the twentieth century, and is shown pictorially in Fig. 3. Without mathematical detail, two points are relevant. Firstly, the total energy emitted per unit time integrated over all wavelengths is proportional to T^4, where the temperature has units of K. Secondly, the wavelength of the maximum in the emission distribution curve varies inversely with T, i.e. $\lambda_{max} \propto T^{-1}$; 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 20 lower, so the Earth's black body emission curve peaks at a wavelength that is 20 times longer or *ca.* 10 μm. Thus the Earth emits infrared radiation with a range of wavelengths spanning *ca.* 4 μm–50 μm, with the majority of the emission being in the range 5 μm–25 μm (or 400 cm^{-1}–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 (6.38×10^6 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 (5.67×10^{-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:

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

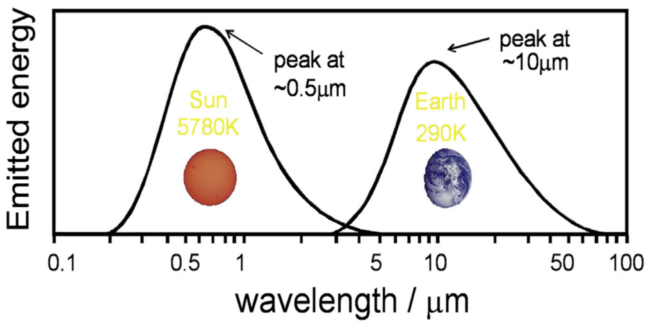

FIGURE 3

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 $\lambda_{max} \propto (1/T)$. The two graphs are not to scale. *(With permission, and adapted from A.M. Holloway, R.P. Wayne, Atmospheric Chemistry, RSC Publishing, 2010.)*

Using the data above, the equation yields a value for T_e of *ca.* 256 K. Mercifully, the average temperature of the Earth is not a Siberian −17°C (256 K), otherwise life would be a very unpleasant experience for the majority of humans on this planet. The one-quarter power in Eqn (1) means that any errors in the values of F_s and A are strongly diluted, so there is not much associated error in the value of T_e. 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 reradiated back toward 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 we should all be grateful. This phenomenon is often called the 'primary' greenhouse effect. It is therefore a complete fabrication of the truth, or a myth, to portray *all* aspects of the greenhouse effect as bad news, and it is the reverse that is true. A relatively simple calculation can show that about 30 K of the 34 K rise in temperature due to primary greenhouse gases is due to H_2O water vapour in the atmosphere, about 3 K is due to CO_2 and about 1 K is due to all the other primary greenhouse gases such as CH_4, N_2O and O_3. Thus the major greenhouse gas by a long way is H_2O vapour and not CO_2. It should also never be forgotten that 99% of the Earth's atmosphere is due to N_2 and O_2, and neither absorbs infrared radiation (see Section 4), so the greenhouse effect is all due to gases that comprise only *ca.* 1% of the Earth's atmosphere. Put another way, our atmosphere is very fragile and sensitive to perturbations in concentration of any of the trace species in the atmosphere that are greenhouse gases.

There is therefore nothing new about the primary greenhouse effect; it has been present for thousands of years, but it is only relatively recently that we have definitive scientific evidence for its presence. Figure 4 shows data from the Nimbus 4 satellite circumnavigating the Earth in 1979 at an altitude outside the Earth's atmosphere. The infrared emission spectrum in the range 6 μm–25 μm

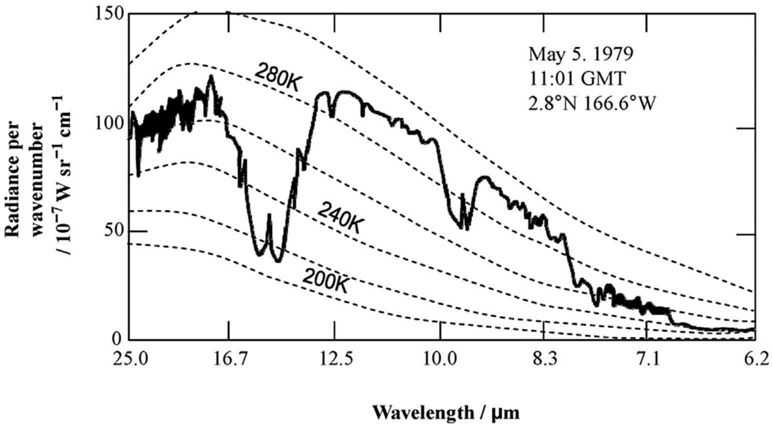

FIGURE 4

Infrared emission spectrum as observed by the Nimbus 4 satellite outside the Earth's atmosphere. Absorptions due to CO_2 between 12 μm–17 μm, O_3 (around 9.6 μm) and H_2O ($\lambda < 8$ μm) are shown. *(With permission from A.M. Holloway, R.P. Wayne, Atmospheric Chemistry, RSC Publishing, 2010; original from R.E. Dickinson, W.C. Clark (Eds.), Carbon Dioxide Review, 1982 (OUP).)*

escaping from Earth represents a black body emitter with a temperature of *ca.* 290 K, with absorptions (i.e. dips) in the radiance per wavenumber data between 12 μm–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, the three major primary greenhouse gases in the atmosphere.

Of course, the argument that the primary greenhouse gases have maintained our planet at a constant temperature of *ca.* 290 K presupposes that their concentrations have remained approximately constant over very long periods of time. As far as we know, this was the case for the primary greenhouse gases, certainly CO_2, up to the start of the Industrial Revolution, *ca.* 1750. However, concentrations of CO_2, CH_4 and, to a lesser extent, O_3 have increased significantly over the following 264 years, and it is the increases 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 the majority of scientists believe we are experiencing today. (Although the concentration of H_2O vapour is much higher, it is not believed that it has changed significantly over the last 260 years, so H_2O is not classed as a secondary greenhouse gas.) That is the main argument of the proponents of the *greenhouse gases, mostly* CO_2*, equal global warming* school of thought. There is no doubt that the concentration of CO_2 in our atmosphere has risen from *ca.* 280 ppmv to current levels of *ca.* 393 ppmv over the last 264 years. (For the physical chemist, 1 ppmv is equivalent to a number density of 2.46×10^{13} molecules cm^{-3} for a pressure of 100 kPa and a temperature of 298 K). It is also not in doubt that the average temperature of our planet has risen by *ca.* 0.6 °C–1.0 °C over this same time window (Fig. 5, the famous *hockey stick*

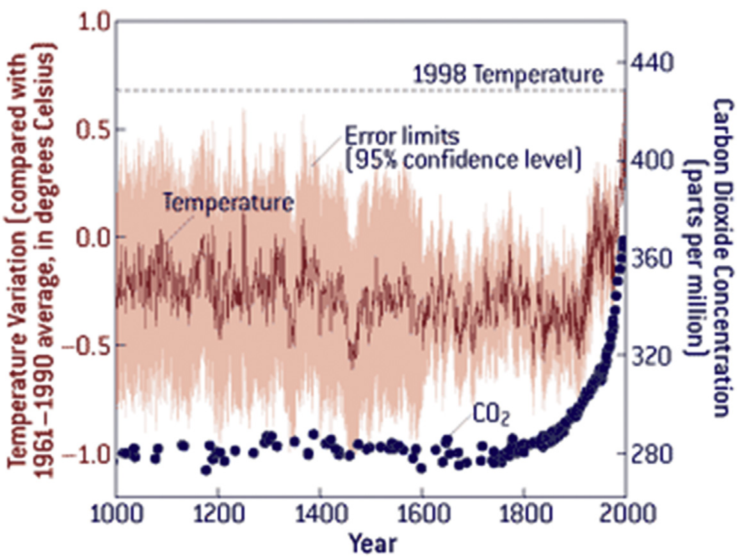

FIGURE 5

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.)* Note: The right-hand-side *y*-axis label should read: CO_2 concentration/μmol mol^{-1}; and the left-hand-side *y*-axis label should read: Temperature variation compared to the 1961–1990 average/°C.

graph, about which whole books have been written). In my opinion, what has not yet been proven in a mathematical and scientific sense 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 (Figure 6), where the correlation *seems* to be better established, will not convince the sceptic. Furthermore, if I was devil's advocate and people did not know what was being plotted on the two axes, I would contend that most, including many scientists, would say there was no clear correlation between the *y* and the *x* data in either Figs 5 or 6. That said, as demonstrated with increasing clarity by the recent IPCC reports, the consensus of world scientists, and certainly physical scientists, is that a strong correlation *does* exist even if it is not possible to prove it mathematically.

By contrast, an excellent example in atmospheric science of sufficient resolution being present to confirm a correlation between two sets of data was published 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. 7) [7]. There was not only

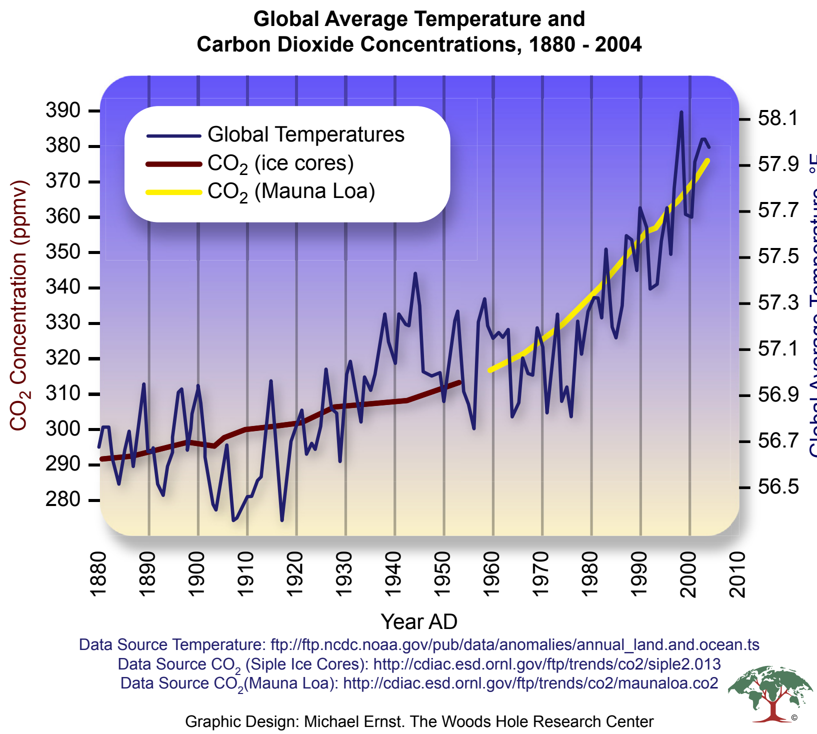

FIGURE 6

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.)* Note, The left-hand-side *y*-axis label should read: Concentration/μmol mol^{-1}; the right-hand-side *y*-axis label should read: Global average temperature/°F. Here t_F/°F = (9/5)(t/°C) + 32.

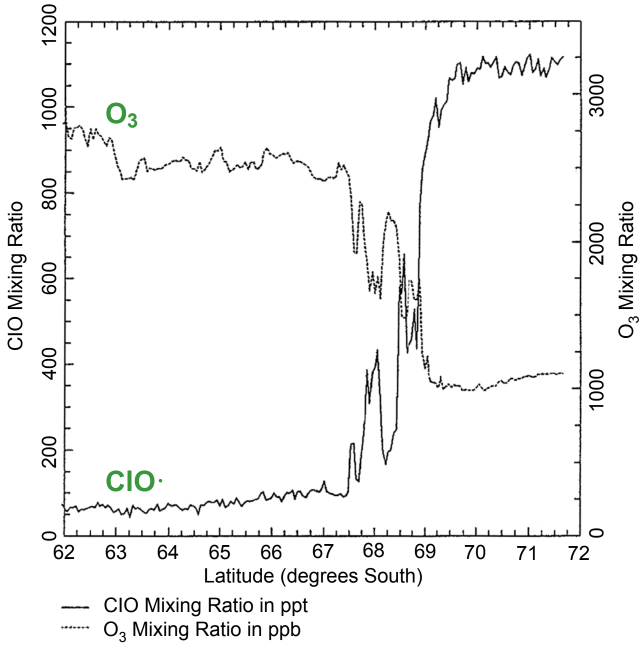

FIGURE 7

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.)* 1 ppb is equivalent to one part in 10^9, 1 ppt to one part in 10^{12}. Note the label on the *x*-axis should read: Latitude/degrees South.

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. When presented with the data, even the most doubting scientist could then accept that the decrease in O_3 concentration in the Antarctic spring was related somehow to the increase in ClO concentration, and over the next 20 years this result led to more research and an understanding of the heterogeneous chemistry of chlorine-containing compounds on polar stratospheric clouds. Unfortunately, such high resolution is not present in the data (e.g. Figs 5 and 6) for the 'CO_2 versus T' argument. This has led to the multitude of theories that are now in the public domain, and the creation of lobby groups on both sides of the argument.

I believe it would be very surprising if there was not some relationship between the rapid increases in CO_2 concentration and the temperature of the planet. In making this statement, the basic assumption remains that the firn measurements from ice core samples of CO_2 concentrations extrapolated back in time are accurate. Nevertheless, there are two aspects of Fig. 5 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 CO_2 concentration increased from 280 to *ca.* 310×10^{-6} 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, the apparent mirroring of increases in both CO_2 levels and T_e over the last 50 years is striking. The most likely explanation surely is that there are a multitude of effects, one of the dominant being 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. That was my position when the first edition of *Climate Change* was published, and it has not changed.

4. THE PHYSICAL CHEMISTRY PROPERTIES OF GREENHOUSE GASES

The basic science of what constitutes an effective greenhouse gas has not changed in the last six years. What follows in this section is therefore only a summary of what I wrote in the first edition. 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 μm–25 μm. Furthermore, since the primary greenhouse gases of CO_2, O_3 and H_2O absorb in the range 12 μm–17 μm (or 590 cm^{-1}–830 cm^{-1}), 9.6 μm (1040 cm^{-1}) and $\lambda < 8$ μm (>1250 cm^{-1}), an effective secondary greenhouse gas is one that absorbs infrared radiation strongly *outside* these ranges of wavelengths (or wavenumbers), yet *inside* the range of 5 μm–25 μm where infrared radiation is present. A molecular vibrational mode is only active in the infrared 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. This is the reason why neither N_2 nor O_2 absorbs infrared radiation since their sole vibrational mode is infrared inactive; they therefore play no part in the greenhouse effect. It is only trace gases in the atmosphere (Table 1) such as CO_2 (4×10^{-2})%, CH_4 (2×10^{-4})%, O_3 (3×10^{-6})%, chlorofluorocarbons such as CF_2Cl_2 (5×10^{-8})% and stable fluorinated molecules such as SF_6 (6×10^{-10})% that contribute to the greenhouse effect. I have already commented that the Earth's atmosphere is particularly fragile if only 1% of its molecules can have such a major effect on humans living on the planet. Furthermore, the most important molecular trace gas, CO_2, 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 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 as a greenhouse gas.

The second property of interest is the lifetime of the greenhouse gas in the Earth's atmosphere – clearly 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, $O^*(^1D)$, and photo-dissociation in the range 200 nm–390 nm in the stratosphere or $\lambda > 390$ nm in the troposphere. Thus, the reaction kinetics of greenhouse gases with OH and $O^*(^1D)$ and their photochemical properties in the UV/visible, will yield important parameters to determine their (deleterious) effectiveness. All these data can be incorporated into a dimensionless number, the global warming potential (GWP), sometimes called the greenhouse potential, 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 therefore one with strong infrared absorption in the windows where the primary greenhouse gases such as CO_2 etc. do not absorb, long lifetimes, and rising concentrations due to human presence on the planet. GWP values of some of the most

Table 1 Main Constituents of Ground-Level Clean Air in the Earth's Atmosphere

Molecule	Concentration/(x or %)		
	x or %	µmol mol^{-1} (ppmv)[a] (2014)	µmol mol^{-1} (ppmv) (1750)
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%	9300	9300
CO_2	3.8×10^{-4} or 0.038%	393	280
Ne	1.8×10^{-5} or 0.002%	18	18
CH_4	1.77×10^{-6} or 0.0002%	1.80	0.72
N_2O	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 8.7×10^{-8}%	0.0009	0
All HCFCs[d]	1.9×10^{-10} or 1.9×10^{-8}%	0.0002	0
All PFCs[e]	8.3×10^{-11} or 8.3×10^{-9}%	0.00008	0
All HFCs[f]	6.1×10^{-11} or 6.1×10^{-9}%	0.00006	0

[a] *Parts per million by volume 1×10^{-6}; 1 ppmv is equivalent to a number density of 2.46×10^{13} molecules cm^{-3} for a pressure of 100 kPa 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] *Perfluorinated molecules (e.g. CF_4, C_2F_6, SF_5CF_3, SF_6, NF_3).*
[f] *Hydrofluorocarbons (e.g. CH_3CF_3).*

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 terms. The data can be quantified and a mathematical description is now presented. The term that characterizes 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 cm^{-1}–2000 cm^{-1}. It is a (per molecule) microscopic property and is usually expressed in the strange units of W m^{-2} ppbv^{-1} (where ppbv refers to parts per 10^9 by volume). If this value is multiplied by the change in concentration of pollutant over a defined time window, usually the 264 years from the start of the Industrial Revolution to the current day, the macroscopic radiative forcing in units of W m^{-2} is obtained. Note that a pollutant whose concentration has not changed over this long time window, such as H_2O, will have a macroscopic radiative forcing of zero. The IPCC 2013 Assessment Report quotes the radiative forcing for CO_2 and CH_4, the two most serious secondary greenhouse gases, as 1.82 ± 0.19 and 0.48 ± 0.05 W m^{-2}, respectively, out of a total for long-lived greenhouse gases of 2.83 ± 0.29 W m^{-2} [5]. (The values in IPCC 2007 were 1.66 W m^{-2}, 0.48 W m^{-2} and 2.63 W m^{-2} [6].) These two

Table 2 Examples of Secondary Greenhouse Gases, and Their Contributions to Global Warming [5,11]

Greenhouse Gas	CO_2	O_3	CH_4	N_2O	CF_2Cl_2 [all CFCs]	SF_6	SF_5CF_3	NF_3
Concentration (2014)/μmol mol^{-1} or/ppmv	393	0.036	1.80	0.32	0.0005 [0.0009]	7.3×10^{-6}	*ca.* 1.6×10^{-7}	9×10^{-7}
ΔConcentration (1748–2014)/ μmol mol^{-1} or/ppmv	113	0.011	1.08	0.05	0.0005 [0.0009]	7.3×10^{-6}	*ca.* 1.6×10^{-7}	9×10^{-7}
Radiative efficiency, a_o/W m^{-2} $ppbv^{-1}$	1.37×10^{-5}	3.33×10^{-2}	3.63×10^{-4}	3.00×10^{-3}	0.32 [0.20–0.32]	0.57	0.59	0.20
Total radiative forcing[a]/W m^{-2}	1.82	*ca.* 0.35[b]	0.48	0.17	0.17 [0.26]	4.1×10^{-3}	*ca.* 9.4×10^{-5}	2.0×10^{-4}
Contribution from long-lived greenhouse gases, excluding ozone, to overall greenhouse effect/%[c]	64 (57)	0 (11)	17 (15)	6 (5)	6 [9] (5 [8])	0.14 (0.13)	0.003 (0.003)	0.007 (0.006)
Lifetime, τ[d]/a	*ca.* 50–200[e]	*ca.* days–weeks[f]	12.4	121	100 [45–1020]	3200	800	500
Global warming potential (100 year projection)	1	–[g]	28	265	10200 [4660–13 900]	23 500	17 400	16 100

Here ppmv is identical to μmol mol^{-1} and ppbv is identical to nmol mol^{-1}.
[a]*Due to change in concentration of long-lived greenhouse gas from the preindustrial era to the present time.*
[b]*An estimated positive radiative forcing of 0.40 W m^{-2} in the troposphere is partially cancelled by a negative forcing of 0.05 W m^{-2} in the stratosphere [5].*
[c]*Assumes the latest value for the total radiative forcing of 2.83 ± 0.29 W m^{-2} [5]. The values in brackets show the percentage contributions when the estimated radiative forcing for ozone is included in the value for the total radiative forcing.*
[d]*Assumes a single-exponential decay for removal of greenhouse gas from the atmosphere.*
[e]*CO_2 does not show a single-exponential decay [9].*
[f]*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 $OH + O_3 \rightarrow HO_2 + O_2$. Its concentration shows large variations both with region and altitude.*
[g]*GWP values are generally not applied to short-lived, i.e. unmixed, pollutants in the atmosphere, due to serious inhomogeneous changes in their concentration.*

molecules therefore contribute 81% in total (64% and 17%, individually) to the global warming effect. Effectively, the radiative forcing value of a greenhouse gas gives a current-day estimate of how serious it is to the environment, but one should appreciate that the value uses concentration data *from the past*.

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

$$GWP_x(t) = \frac{\int_0^t A_x(t).dt}{\int_0^t A_{CO_2}(t).dt} \tag{2}$$

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 28 times as serious as CO_2 for global warming, what they are saying is that the GWP_{100} value of CH_4 is 28; one molecule of CH_4 is therefore expected to cause 28 times as much 'damage' as one molecule of CO_2. Within the approximation that the greenhouse gas, x, follows a single-exponential time decay in the atmosphere, it is possible to parameterize Eqn (2) to give an exact analytical expression for the GWP of x over a time period t [8]:

$$\frac{GWP_x(t)}{GWP_{CO_2}(t)} = \frac{MW_{CO_2}}{MW_x} \cdot \frac{a_{0,x}}{a_{0,CO_2}} \cdot \frac{\tau_x}{K_{CO_2}} \cdot \left[1 - \exp\left(\frac{-t}{\tau_x}\right)\right] \tag{3}$$

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}, a measure of the non-single value of the lifetime of CO_2, which can be calculated for any value of t [9]. It can be seen that 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 have caused criticism by Shine et al. of the use of GWPs in policy formulation [9]. Note that a similar equation to (3) given by Mason et al. has numerous typographical errors and should be disregarded [10].

Data for eight greenhouse gases are shown in Table 2. (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 $\times 10^{-6}$ by volume) over different parts of the Earth, and the average lifetime is only a few days. Since its average global concentration has not changed significantly since the middle of the eighteenth century, it has zero radiative forcing and is not included in this table.) CO_2 and O_3 are naturally occurring greenhouse gases whose concentration levels ideally would have remained constant at pre-Industrial Revolution levels. The a_o value of O_3 is over three orders of magnitude greater than that of CO_2, but its tropospheric concentration is four orders of magnitude lower. CH_4 and N_2O constitute naturally occurring greenhouse gases with a_o values intermediate between that of CO_2 and O_3. The CH_4 concentration, although small, has increased by *ca.* 150% since preindustrial times. After CO_2, it is the second most important greenhouse gas, and its current total radiative forcing is *ca.* 26%

that of CO_2. N_2O concentration has increased only by *ca.* 18% 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, anthropogenic 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 a number density of 2.46×10^{10} molecules cm^{-3} at a pressure of 100 kPa and a temperature of 298 K. Their concentration is now decreasing due to the 1987 Montreal and later international protocols introduced to halt the destruction of stratospheric ozone. It is ironic that these decisions were taken with no regard to their (beneficial) effect on the issue of 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. NF_3 is a long-lived fluorinated compound that was discovered in the atmosphere since the first edition of this book was written [12]. Its properties are shown in the last column of Table 2. It was not included in the Kyoto Protocols of 1997 listing which greenhouse gases should be included for long-term monitoring [13], but there is now near-universal agreement that it should be included in future protocols from follow-up meetings, e.g. Paris in 2015.

It is noted that CO_2 and CH_4 have the lowest GWP values of all the greenhouse gases listed. 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 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 large change in atmospheric concentration since the Industrial Revolution; note, however, that the a_o and GWP values of both gases are relatively low. By contrast, the SF_5CF_3 molecule has the highest microscopic radiative efficiency of any known greenhouse gas (earning it the title 'super' greenhouse gas [8,14]), 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 years have tracked each other closely [15]. The GWP of these two molecules is very high, SF_6 being slightly higher because its atmospheric lifetime, *ca.* 3200 years [16], 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 cm^{-3} at 100 kPa 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 – ultimately, I believe, population levels on the planet (see Section 5.3). The *microscopic* properties of these compounds, however, are controlled by factors that students worldwide 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.

In the first edition of *Climate Change*, a major section of the chapter described how the lifetime of a greenhouse gas was defined, particularly for a long-lived pollutant such as a perfluorocarbon molecule where lifetimes are quoted as several hundreds to thousands of years. In 1994, Ravishankara and Lovejoy made the bold statement that 'all long-lived molecules should be considered guilty [on their potential impact on the earth's atmosphere] until proven otherwise' [17]. Their example to justify this policy was that of anthropogenic chlorofluorocarbon molecules, produced in increasingly large quantities from the 1930s for the next four decades for industrial and domestic purposes when these molecules were thought to be innocuous. The pioneering work of Molina and Rowland in the 1960s and 1970s showed that these long-lived molecules with lifetimes of several hundreds of years were unfortunately having an unforeseen deleterious effect on the ozone layer in the stratosphere [18], and ultimately led to the Montreal Protocol of 1989 and the phasing out of these molecules from production [19]. In many ways, this was a wonderful example of the power of science and scientists to convince politicians that action was needed, and the latter responded accordingly. The latest predictions are that the ozone layer in the stratosphere will recover to its levels of *ca.* 1950 within the next 50 years–100 years, and the problem created by these molecules will have been reversed [20a–20c]. Many scientists now believe that the issue of carbon dioxide concentrations and global temperature is the modern-day scientific equivalent, but are thinking words to the effect *if only the problem was so easy to solve with carbon dioxide and global warming*.

In the final section of this chapter, I move away from the science of greenhouse gases and global warming. I contend that the scientific case is now so strong and accepted by 99%+ of the world's scientists that, as a population of *ca.* 7 billion people living on this planet, we must take ownership of this issue and come up with potential solutions. Of course, there are still inconsistencies in some of the data, and some aspects of the infamous hockey stick graph (Fig. 5) are unexplained. But this should not blinker us to the major environmental issue that needs to be addressed.

5. HAS ANYTHING CHANGED IN THE LAST DECADE?

This is a deliberately provocative question to ask. I answer it in three sections, as it is applied to (1) the science of greenhouse gases and possible global warming, (2) public perceptions of greenhouse gases etc. and (3) action at the private and the political level.

5.1 HAS THE SCIENCE CHANGED?

The simple answer must be no. The data presented in the two tables are taken, in the main, from the IPCC Fifth Assessment Report of 2013. Some of the radiative efficiencies, radiative forcing, lifetimes and GWP values have improved and become more accurate with lower quoted errors. A few new long-lived greenhouse gases, such as NF_3 and perfluorotributylamine, $N(C_4F_9)_3$, have been discovered in the atmosphere [12,21]. But the essential message remains that the net radiative forcing of the atmosphere due to long-lived greenhouse gases is increasing slowly (2.43 ± 0.24 W m^{-2} from the third United Nations IPCC report of 1998, 2.63 ± 0.25 W m^{-2} from the fourth report of 2007, and now 2.83 ± 0.29 W m^{-2} from the fifth report of 2013), with the predominant contributors being CO_2 (*ca.* 60%) and CH_4 (*ca.* 18%). Whilst all other long-lived greenhouse gases contribute a not-insignificant *ca.* 20% and keep atmospheric scientists busy with requests for more money to study their properties, the radiative forcing budget is dominated by CO_2 and CH_4 emissions. Furthermore, the increasing concentration of CO_2 in the atmosphere shows no sign of slowing down, with the current value very close to the emotive level of

400×10^{-6} by volume (400 ppmv). There is nothing special about this number per se, but the general view of climate scientists is that if this value gets close to 500×10^{-6} (500 ppmv) by volume, the Earth's atmosphere will have reached the point of 'no return', and it will be close to impossible to stabilize the temperature of the planet; this is often referred to as the *runaway greenhouse effect*, caused by positive feedback of increasing temperature causing increasing concentrations of water vapour, which cause ever-increasing temperature rises. Put in starker terms that nonscientists may find easier to understand, the concentration of CO_2 in the atmosphere has already increased over halfway from pre-Industrial Revolution times, *ca.* 280 ppmv, to the level, *ca.* 500 ppmv, that will have major consequences on the way the huge majority of us can live on this planet. However, modellers also predict that if the CO_2 concentrations can be stabilized at the current levels of *ca.* 400 ppmv by 2020, then reduced to less than half of 1990 levels by 2050, and continue to be cut thereafter, then the rise in temperature of the Earth from preindustrial times to the end of the twenty-first century may be limited to around 2 K. It is generally believed that most countries should be able to adapt to cope with this increase. Anything higher and the future will become increasingly bleak, which is a sobering thought.

5.2 HAVE PUBLIC PERCEPTIONS OF GREENHOUSE GASES, ETC. CHANGED?

This is a more difficult question to answer, and any response must be subjective. But my general view is that this *is* an issue that is getting into the psychology of the general public, even if opinions can swing with alarming rapidity. The international convention in Copenhagen, Denmark, in 2009 attracted huge publicity worldwide, even if it did not result in much tangible action [22]. However, my overriding impression from television remains that of President Obama jetting into the country in Air Force 1, the US presidential aircraft, and jetting out 24 h later, rather missing the point that air travel is a major component of carbon emissions. The power of the Internet increases exponentially with time and is now one major component of attracting multimillion petitions putting pressure on national governments to act. Unfortunately, bad publicity can halt any positive momentum that has been built up, so reports in 2010 that the University of East Anglia in the UK might have suppressed emails and reports suggesting that the issues around global warming were not as serious as was being made out, were hugely damaging. This was then reflected in opinion polls immediately afterward that global warming was now not a major issue of concern to the individual or the state, thereby reversing the trend that polls had been showing post-Copenhagen.

At a national level, Europe is leading the way and the UK has much to be proud of. For example, the UK government of the day in 2008 legislated to commit the country to a target of reducing greenhouse gas emissions by the year 2050 to less than 20% of the levels they were at in 1990, with an interim target of reducing CO_2 emissions by 2020 to less than 74% of the level in 1990 [23]. Targets are all very well and good, but nobody seems to have said what will happen if this target is not met 36 years from now, or it is clear by, say 2025, that the target will not be met. In October 2014, the European Union Council of Ministers, of which the UK is one of 27 members, committed to reduce CO_2 emission to less than 60% of 1990 levels by the year 2030, and to produce at least 27% of its energy from renewable sources and not from fossil-based fuels [24]. The former target is not dissimilar to that enshrined in UK law in 2008, but it applies to a much larger population and countries with a range of economies so its impact should not be dismissed. The EU hopes that this will lead to the same reduction as legislated by the UK, i.e. a reduction by 2050 to less than 20% of the levels in 1990. The quoting of statistics in such percentage terms can seem rather bland and is at times not very useful. These commitments are therefore expressed slightly differently in units of *metric tonnes of* CO_2 *emitted per person per year.* This is not exactly the most SI of units, but it is convenient to use because the absolute values are finite, involve no large powers of 10, and should therefore be understandable by the public. In these units the UK average at the moment is about 14, the US average about 23, and the global average about 6. The UK's target for 2050 is about 3 and the EU's target for 2030 is about 4. Modellers predict that to avoid the worst effects of climate change in the next 100 years, i.e. to limit the increase in global temperatures to less than 2 K above that in preindustrial times, the present global average emission must drop from about 6 to below 1.5. *By any standards, these are huge changes.* In November 2014 President Obama finally committed the USA to a major reduction of greenhouse gases, but only time will tell whether his policies can be worked through to positive action given that for the last two years of his presidency the US Senate will be controlled by the opposition Republican party. The two largest populations in the world, China and India, have yet to declare any binding targets. This is sad, because the overriding reaction I hear from Europeans who think about these issues is words to the effect: *what difference will anything I do as an individual make to this global problem, when China's emissions [especially] are so huge compared to those of Europe?* I believe that a binding target set by these countries would help Europeans believe that they were taking the issue seriously and might help individuals in Europe do more themselves. One should not forget that it is the rich and industrialized first-world countries in the West that have, in the main, created the problem.

But perhaps most encouraging for the future, the mantra of the developed world for the last 50+ years has surely been that we must maximize *growth*, however that is defined, in all countries; only then will we prosper. For the first time, in the last decade when the science of global warming has become increasingly robust, I believe that many influential people are publically challenging this premise. Such people are asking *why* is growth the paramount factor if it is leading to a planet that will be a very unpleasant place to live within the next 100 years? This is almost a heretical view to take of criteria we should use (or *not* use) to define our position in the global world, and it turns the world of politics and economics on its head. I contend, however, that potential global warming is the *ultimate* global issue simply because it has the potential to affect every person on this planet. Therefore, it is right to think anew and, if necessary, challenge the criteria on which countries have based their policies and lifestyles in the past.

5.3 WHAT ACTIONS HAVE BEEN TAKEN AT THE PRIVATE AND THE POLITICAL LEVEL?

Here my perception is that the message is mixed. An outpouring of guilt certainly will get us nowhere. To counter such negativity, many examples of excellent practice are emerging at an individual level, certainly in the UK. For example, conservation of energy through double glazing and roof insulation of housing, generation of solar electricity through roof-mounted photovoltaic panels, the trend to driving smaller and more fuel-efficient cars (and perhaps electric cars will be the norm in 50 years' time), and the increase in bicycling and walking as a long-term lifestyle change that healthy people should be making are just four examples. But I suspect that these examples are just scratching at the scale of the problem, and almost inevitably it is the educated 'converted' class who are taking these actions. I do believe that national policies must be imposed, and although it goes against the instincts of politicians of all colours to *tell people how to live their lives*, I fear that this is exactly what they must do. And because this is an issue with the potential to affect the lives of every person on this planet, unlike any other world phenomenon in my lifetime except perhaps the Cuba crisis and the possible outbreak of nuclear war in 1961, global solutions are needed and the normal 'rules' of economics cannot apply. So I fail to see how any attempts to trade in carbon, i.e. the 'transfer' through payment of emissions to other countries, can possibly succeed. It is a short-term solution of dubious morality to a long-term global problem, and is doomed to fail.

Others in this book may write much more knowledgeably than I can about possible ways to (1) change our energy policy to become less reliant on the burning of fossil fuels, (2) ways to trap emissions of greenhouse gases, and possibly (3) engage in geoengineering to reduce incoming radiation from the sun as a means to control our increasing temperature. Under category (1) must fall a renaissance in nuclear energy, and possibly the huge expansion of fracking, which is the release of shale gas reserves from deep within rocks. Whenever the former policy seems to be gaining favour, a serious accident, such as that at Fukushima in northern Japan in 2011, can set the clock back by at least a decade. Soon after this event, Germany changed dramatically to a nuclear-free energy policy, and the UK has not yet committed to a big expansion in this technology that seemed likely in the preceding 10 years before 2011. The risks involved in following the latter policy of fracking are significant, if only because of the huge increases in methane gas in the atmosphere that are likely to happen; nothing can change the basic science that one molecule of CH_4 has the potential to cause about 28 times as much damage to the world's climate as one molecule of CO_2 over the next 100 years. However, the potential benefits are considerable. Categories (2) and (3) can be interpreted as possible solutions to a problem that has been allowed to develop unchecked. I believe it is more sensible to follow the advice of Ravishankara and Lovejoy [17], and reduce the amounts of emissions of damaging greenhouse gases into the atmosphere in the first place. In simple terms, use less energy.

I divide possible solutions into three sections: (1) relatively easy to implement, however painful, (2) much harder to implement, but surely possible if the world is serious about this issue, and (3) incredibly complex world issues that must be addressed, probably by the United Nations.

5.3.1 Easy to Implement and Solve

Six years ago, I wrote that nobody wants to or can turn back the clock on scientific progress [1]. The challenge therefore to reducing our dependence on fossil fuels and save energy is to devise policies that may seem retrospective but do not reduce the standard of living of the population and negate all the benefits that technology has brought us in the last 200 years. An excellent book, *Sustainable Energy – Without the Hot Air* written by MacKay in 2009, available free on the Internet, shows where the UK emissions come from at a personal level [25]. On average, every person in the UK uses 125 kWh of energy per day, after metric tonnes of CO_2 per person per year the most commonly used unit of carbon currency. It is surely stating the obvious that any policies advocated cannot possibly apply to every person in a developed country, and in general the young, the old, the disabled and the infirm will be exempted. That said, MacKay estimates that wearing more clothes and turning down thermostats by a degree or two both at home and work might reduce this figure by about 20 such units; stopping flying might cause a reduction of 35; generally modifying our means of transport within the UK by driving less and biking or walking more might reduce this figure by about 20; avoiding packaging and the buying of clutter, however that is defined, might, to my surprise, cause a huge reduction of 20; and becoming vegetarian might cause a reduction of 10 kWh per person per day. These are all big percentage changes, even though one accepts that there are huge errors in the numbers estimated. It is a reasonable question, however, to ask which of these could be turned into UK national policies, with exceptions built in for vulnerable groups.

In the first edition of *Climate Change*, I advocated a reversal of the 1991 change of legislation in the UK that allowed for Sunday trading for 6 h d^{-1} (where d refers to day) in all shops. I noted that Sunday closing was still the law in Switzerland, but it remains one of the richest European countries by whatever criterion is applied. It is accepted that lifestyles in the UK would have to adapt from what many of us have become used to in the last 23 years, but I believe this is one of the easier national policies to make and implement. It would presumably reduce the energy consumption of UK shops by about one-seventh or 14%. I also advocated a reduction in domestic air travel within a small country such as the UK, with a corresponding increase and investment in rail travel. That is indeed what is happening with the proposed High Speed 2 (and possibly HS3) train routes from London to the north of England and possibly Scotland. Only time will tell if this leads to a big reduction in domestic air travel. I also cannot be the only person to question whether so much international long-distance air travel for business meetings is really necessary, and whether technology can assist. The concept of Skype for 1:1 face-to-face discussions can surely be extended so that 100 people can meet remotely without the need for travel, and indeed early versions of such software (e.g. Visimeet) are now available [26].

Many other policies could be rolled out quickly. Two examples might be free insulation of roofs and double glazing in *all* domestic housing, and a huge investment in cycle routes to make the bicycle a safer and more child-friendly means of local transport. It also seems reasonable to ask whether the minimum working temperature for employees could be reduced from its current level of 16°C (289 K) by a degree or two; often the working temperature in offices is higher. MacKay estimates the savings in energy could be substantial [25], and he is effectively asking whether it is necessary to live in shirtsleeves and the female equivalent for most of our waking hours. Has health and safety legislation become so sacrosanct that external packaging on much food sold in the supermarkets is quite unnecessary, leading to what MacKay calls excess 'clutter'? In the first few years of this century, the UK government announced that civil servants in all the major departments of the state would ensure that future legislation was checked for its impact on the environment. I see little evidence that this has happened. It is also a pity that this policy did not extend back to legislation passed in the last 30 years–50 years. For example, I do not believe that anyone thought of the environmental effects of allowing a free-for-all when the provision of compulsory state education was deregulated by the 1988 Education Act. This decision effectively led to the abolishment of local catchment areas for schools in the cities to which pupils walked, and the 'school run' by car became part of the UK vocabulary. The present UK government of a different colour, when elected in 2010, claimed to become one of the greenest ever elected. Unfortunately, I see little evidence that this claim from either can be substantiated. By my criteria, the above changes in the last two paragraphs are relatively easy to make, they may lose a few votes and be painful for some individuals, but ultimately I believe that they have to be made if we wish to control carbon emissions.

5.3.2 Moderately Difficult to Implement

The unit of carbon emission that everyone would understand is the cost to their financial pocket. Perhaps all developed countries should move rapidly to a system of taxation whereby the principle of *the polluter pays* becomes paramount. In our technological world, this could mean that everyone has a carbon credit card, paying, presumably, a premium for excess gas and electricity domestic bills, for petrol and use of the roads, and certainly for air travel. Again, this was an idea proposed by the Labour Government in the UK about 10 years ago, but was dropped when it was decided that it would be too difficult to implement and public reaction was negative, to say the least, from the day it was tentatively suggested. The prime minister of the day infamously said that climate change was not going to be solved by everyone stopping flying, a statement that might have won him support from many newspapers but caused many scientists to raise eyebrows in some exasperation.

A different issue concerns food production, what we eat, and where the food comes from. The more anyone looks at the issue of the supply chain, and especially the huge number of miles that food often travels between source and consumption, the more baffled they become. The organic movement and localism have started to address these issues at a microscopic level, but I sense that their contributions will be negligible unless the large multinational supermarkets embrace these concepts. For the last 50 years, I would suggest that the concept of the individual/customer having the paramount right to eat food at the cheapest price has swept aside any environmental consequences, and I believe that this has to change over the next 50 years. We will almost certainly have to pay more for food in real terms, but that is the price to pay for addressing the issue of excess use of fossil fuels for unnecessary travel. One should then address what we eat. Cattle use a lot of our limited land for grazing, and there is an argument that we should reduce meat consumption, if not become vegetarians of whatever strictness – a policy effectively being advocated by MacKay [25] – thereby also reducing methane emissions. The growth of genetically modified crops must surely be allowed to continue, as I do not believe that the perceived risks have materialized. We may then reduce our dependency on cattle as a source of food.

These are two areas of policy that apply to all developed countries, and different places will implement different means to tackle them. On my scale, however, these qualify as moderately difficult issues to solve, but such painful projects must be addressed if the planet is going to be a pleasant place to live for the majority of its population.

5.3.3 Very Difficult to Solve

There is one overriding issue that dominates all else in this category and that is the population of the planet. The figures are stark. Fifty years ago the population was 3.3 billion (3.3×10^9), today it is 7.3 billion, and it is predicted to rise close to 11 billion by 2100, with the large majority of this expected growth occurring in Africa [27]. Whilst currently 75% of the world's population live in Asia and Africa, that figure is predicted to grow to 82% by the end of the century. Conversely, the population of Europe is predicted to fall from its current level of 11% (or 0.74 billion) to 6% (or 0.64 billion). All of these people will need to be housed and fed. CO_2 and CH_4 currently contribute about 81% of the total radiative forcing of long-lived secondary greenhouse gases (Table 2), but I believe that it is too simplistic to say that control and reduction of CO_2 levels will be the complete solution. It is my personal belief that CO_2 levels in the atmosphere correlate loosely with lifestyle of many of the population, and with serious effort, especially in the developed world, huge reductions are possible; examples are given in Sections 5.3.1 and 5.3.2 above. 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 remains surprising and unclear why the radiative forcing of methane, 0.48 W m^{-2}, has been unchanged over the last two decades [5], a major component of methane emissions correlates *strongly* with the number of animal livestock, which itself is dependent on the population of the planet.

If this point is accepted, then population control on a worldwide scale must be openly discussed and the subject cannot be avoided if we are to control methane emissions. This is one area of policy where even the most outspoken of politicians in any country is reticent to go, and apparently simple policies can often have unforeseen consequences decades later. For example, China introduced its one-child-per-family policy over 30 years ago; it has had some of the desired effects on population levels in their large cities, but there are social consequences that are only now beginning to manifest themselves; for example, who will look after the old as their population ages? The message, if there is one, coming from Western countries, is mixed. Europe and the US have always believed in the absolute right of individuals to make this choice independent of the state, but it is not difficult to see how governments in any country could influence peoples' way of thinking by limiting financial access to the (welfare) state once families get above a certain size. That said, family sizes in the West decreased significantly once contraception became freely available in the 1960s, but no government wants population levels to drop too much because of the inevitable loss of revenue from taxation; Japan is currently worried about how few children are being born in their country for just this reason. Conversely, the leaders of the Catholic Church, at least in public, will not discuss the matter, believing in the absolute sanctity of life and refusal to accept any form of contraception, whilst the huge majority of its members, if surveys are to be believed, mercifully leave its rulings on the floor as they close the bedroom door.

Controlling the increase of, let alone reducing, world population levels is a huge area of policy that calls for intergovernmental agreements at all levels. It will call for much patience and understanding of how others lead their lives in different continents, a 'one-size-fits-all' policy simply will not work, and many compromises from positions that are currently viewed as *nonnegotiable* or *the red line over which we will not step* will be needed. For all its faults and decreasing respect with which it is viewed as a global organization, I see no alternative to the United Nations leading on such issues, and surely this should be their major policy directive for the next few decades. It is simply not possible to separate the issue of person-made climate change/global warming from that of world population, and true leadership at the world level is surely needed to help bring about this change in public perception.

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