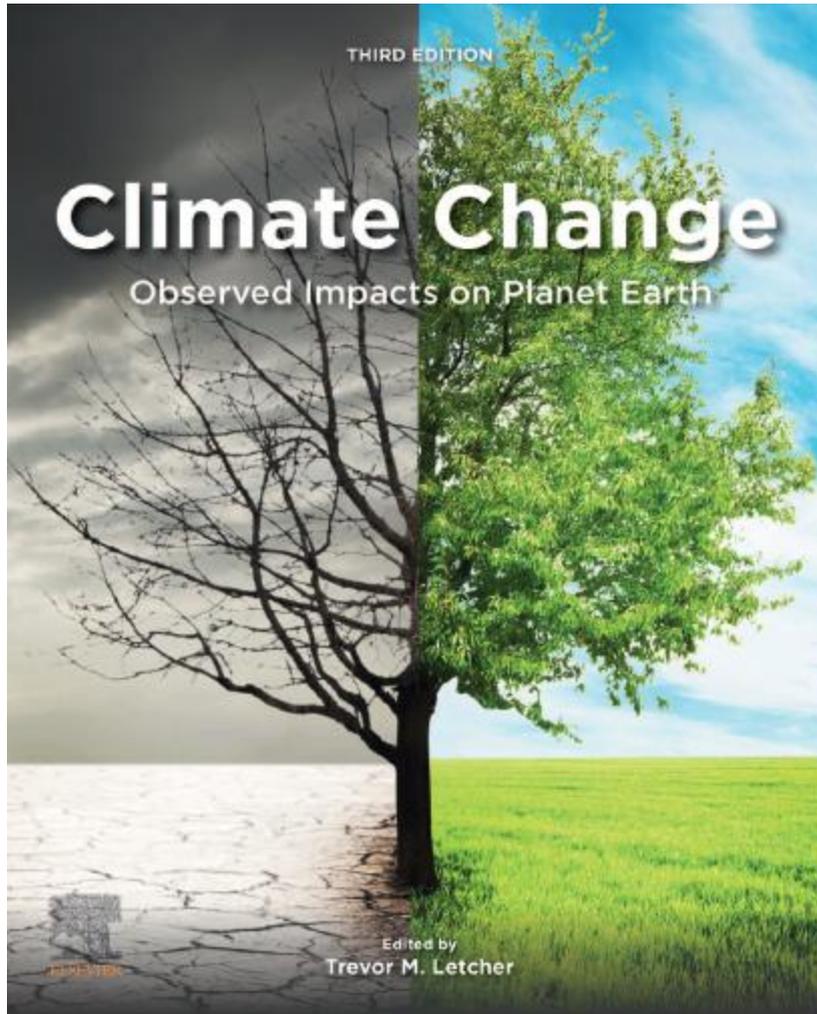


THIRD EDITION

Climate Change

Observed Impacts on Planet Earth



Edited by
Trevor M. Letcher

CLIMATE CHANGE

OBSERVED IMPACTS ON PLANET
EARTH

THIRD EDITION

Edited by

TREVOR M. LETCHER

Emerita Professor, School of Chemistry, University of KwaZulu-Natal, Durban, South Africa



Greenhouse gases and the emerging climate emergency

Richard Tuckett

School of Chemistry, University of Birmingham, Birmingham, United Kingdom

1. Introduction

This is the third edition of *Climate Change: Observed Impacts on Planet Earth*, and therefore, the third time I have written about greenhouse gases and their contribution to climate change. Times have changed hugely since the first edition was published in 2009. Then, it seemed to me that it was not possible to prove, in an absolute and scientific sense, any correlation between CO₂ global concentrations and the average temperature of planet Earth. The result was that mixed messages were being portrayed to the general public. In the second edition written six years later [1], I posed three questions. First, had the basic science since 2009 changed? Second, what change had there been in public perceptions about possible global warming? Third, were any direct actions or policies being developed about possible global warming? In retrospect, what I wrote in 2015 included policies that I suggested be implemented at individual, government, and intergovernment levels. Five years later, although the science base has not changed at all, public perception definitely has changed. First, the language now used is much stronger; global warming has become *global heating*, a climate skeptic has become a *climate science denier*, and most significant climate change has become *climate emergency*. Second, climate science deniers have all but disappeared from the mainstream media channels in all developed countries; alas, there is one notable exception, the current President of the United States of America. Third, media attention worldwide is now upon pressure groups such as Extinction Rebellion and individuals such as Greta Thunberg; whatever the reader's personal views about the methods of communication developed by such pressure groups and this individual, nobody can surely deny that their combined influence throughout the world has been nothing short of awesome.

With the one exception mentioned earlier, if there is one phrase that is now commonplace from government leaders of all colours, it is that we must “*trust the scientists.*” Never has atmospheric science or the people practising this profession been held in such high regard! Reports or television programs seem to come out almost weekly about the current state of the climate, and what will happen if actions are not taken to alleviate increasing concentrations of greenhouse gases, especially CO₂ and CH₄, over the next 30–50 years. Examples are the Future of Planet Earth (September 2017, [2]), the Earth’s Energy Imbalance (August 2019, [3]), a special United Nations Intergovernmental Panel on Climate Change (IPCC) report on the Oceans’ Cryosphere (September 2019, [4]), the State of the Climate 2018 (published in September 2019, [5]), and probably most significant United in Science (September 2019, published days before the emergency UN meeting for all world leaders (*and Greta Thunberg!*) in New York, [6]). Since the second edition of *Climate Change* was published, I have written a detailed description of the science of greenhouse gases in the third edition of *Encyclopedia of Analytical Science* [7], and it therefore seems appropriate to summarize the most up-to-date scientific data in this chapter for *Climate Change*.

It is important to make three caveats at the onset. First, the basic science has not changed, the only major changes year on year being the increasing concentrations of greenhouse gases and the combined radiative forcing of such species. Second, for the general public, error analysis still remains a misunderstood concept; so while it is normal for atmospheric scientists to appear cautious with public statements by quoting errors in their numbers, this is an alien concept to the nonscientist in the street who wants to hear absolute certainties. Third, although most of the media attention is now focused on the increasing concentration of CO₂, other greenhouse gases, especially CH₄, have the capacity to cause significant long-term damage to the environment, a point consistently made by Shine [8]; currently, 34% of the contribution to the overall secondary greenhouse effect is due to gases other than CO₂. At a personal level, it is worth noting that I only got into this area of science by accident in studying the ionization properties of perfluorinated compounds such as CF₄, SF₆, and CF₃SF₅ [9]. Twenty years on, we now know that they are all potentially serious secondary greenhouse gases having exceptionally long lifetimes in the atmosphere, many hundreds if not thousands of years. While their concentrations currently might still be fairly small, they have the capacity to cause serious problems if their concentrations, especially SF₆, are allowed to increase in an unchecked manner.

I conclude this chapter with what I perceive as some simple-to-implement, some difficult-to-implement, and finally some incredibly complex issues that must be addressed if this huge threat to civilization is to be controlled. I sketched these out in 2015 in the second edition of *Climate Change*. Here, I expand these ideas, published briefly one year ago in the Elsevier online reference database, *Earth Systems and Environmental Sciences* [10]. And if any reader does not realize the seriousness of the situation, perhaps the most worrying aspect of the climate emergency is the very rapid temperature increase in the Arctic and Antarctic at the two Poles, much more rapid than was predicted even as recently as 20 years ago. If this increase continues leading to rising sea levels throughout the world, swamping of major cities becomes a definite possibility. Then, global migration of people, probably from the low-lying countries of the Southern Hemisphere to high-lying countries in the Northern Hemisphere, will happen on a scale that will make the current migration issues in Europe seem miniscule.

2. Myths about the greenhouse effect

There are several myths that have grown into the conscience of the general public on this subject. I highlight the two most serious. First, there is a general belief 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 a Siberian winter, i.e., -17°C (256 K). Second, and perhaps the more serious myth, the large majority of the world’s population regard *weather* and *climate* as the same phenomenon; even the current President of the United States makes this elementary mistake. 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 should we wear? The latter is a 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 United Kingdom was very cold, there is no problem ahead; seven years ago, I heard such prejudice with disturbing regularity. Now that the more recent years of 2006–2018 have been recorded as some of the hottest in the past 100 years, and indeed, 20 of the last 22 years globally are the hottest on record [11], this sort of language is mercifully disappearing.

What facts are indisputable? First, nobody can surely argue with the observation, made at many observation points, usually in clear-air remote coastal sites around the world (e.g., Fig. 2.1), that CO_2 concentrations are increasing relentlessly, year by year, and the average value for 2018 was 407.4 ± 0.1 parts per million by volume (ppmv) [5], the highest ever recorded. The value in preindustrial Britain was c.278 ppmv, and if ice core (i.e., firm)

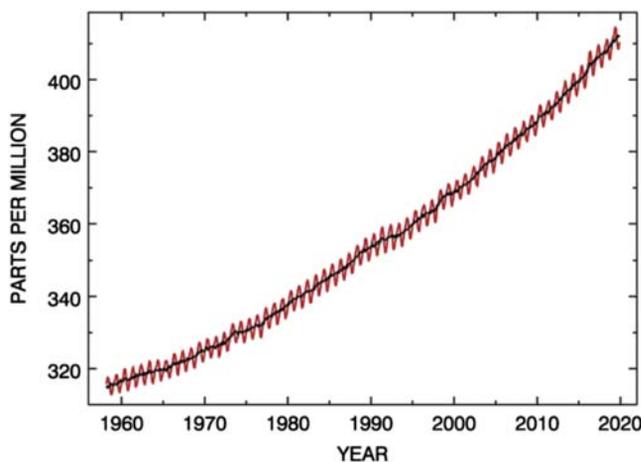


FIGURE 2.1 The increasing levels of CO_2 in the Earth’s atmosphere over the past 60 years. Data were recorded at the Mauna Loa Observatory in Hawaii, and they highlight the relentless increase in concentration year by year. The small oscillations every six months are caused by seasonal changes due to 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 / $\mu\text{mol}/\text{mol}$. With permission from www.esrl.noaa.gov.

measurements are to be believed we have never had the current level of CO₂ concentration in the Earth's atmosphere for the past c.800,000 years. Note that the small 6-monthly oscillations in the data (Fig. 2.1), typically ± 5 ppmv, are caused by seasonal changes due to photosynthetic activity of vegetation which consumes CO₂; oscillations reduce when the recording station is located in a region with scarce vegetation, e.g., Antarctica. There is now a worldwide array of such instrumentation, the results are shared between the communities, and the results are remarkably consistent. The US Environmental Protection Agency (EPA) collates all the data, updated annually [12]. Data are analyzed in a slightly different way by the United Nations IPCC Assessment Reports every 5–7 years, the next one (the sixth) being due in 2021, but the main results are not essentially different. Furthermore, the concentrations of other long-lived greenhouse gases such as CH₄ and N₂O are also increasing year on year, as reported since 2006 with great accuracy by the World Meteorological Organization Greenhouse Gas Bulletins [13]. The most recent data for CH₄ and N₂O from 2018 give their current average concentrations as 1.858 ± 0.001 ppmv (up from 0.72 ppmv in preindustrial times) and 0.331 ± 0.0001 ppmv (up from 0.270 ppmv), respectively [5]. If percentage increases are important numbers for policy makers, the increase in concentrations of the three most significant secondary greenhouse gases, CO₂, CH₄, and N₂O, since the start of the Industrial revolution is therefore 47%, 158%, and 23%, respectively. Second, the evidence is strong that average global temperatures are also rising; it has risen somewhere between 0.9 and 1.1°C since the early years of the Industrial era (i.e., after c.1750 AD), Fig. 2.2, but the certainty level in this statement is lower because of greater uncertainty in the data. Third, the region of the Earth's atmosphere where global warming occurs is the troposphere, the first c.10 km of altitude above the Earth's surface. Yet this is the region of the atmosphere where

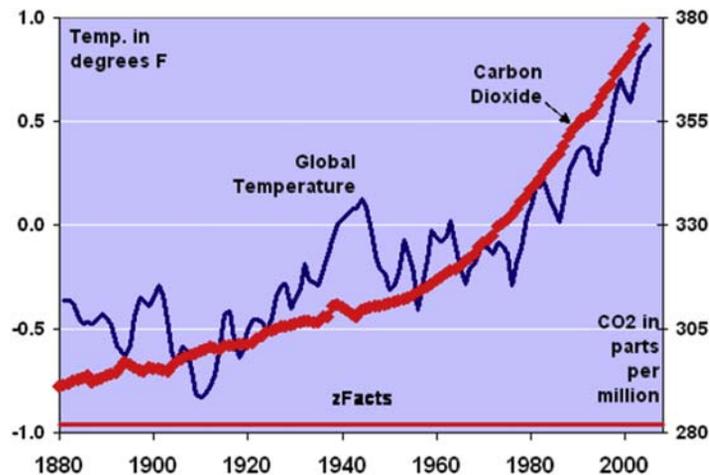


FIGURE 2.2 The average temperature of planet Earth (in blue) and the concentration level of CO₂ in the Earth's atmosphere (in red) during the past 130 years. A rise of 1 F is equivalent to 0.56°C. The article by Hocker, see below, even suggests that it is the temperature rise that is causing the increase in CO₂ concentration, not the other way round. Note: This figure, slightly adapted, was used as the front cover picture of *Climate Change, Observed Impacts on Planet Earth*, Second ed., (2015). With permission from Stoft <http://zfacts.com/p/226.html> and Hocker <http://wattsupwiththat.com/2010/06/09/>.

both homogeneous and heterogeneous processes take place, including reactions on aerosol surfaces, and the chemistry of this region is probably the least well understood. Fourth, while the large majority of world scientists now believe that there *is* a correlation between the increasing CO₂ concentration and the very probable rise in the Earth's temperature, from a mathematical point of view, it is difficult to *prove* this correlation because there is not sufficient signal-to-noise ratio and/or resolution in the data. Indeed, being devil's advocate, if the axes labels in Fig. 2.2 were removed and the graphs only were displayed, most scientists would surely say that the two data sets displayed on the *y*-axis in red and in blue *might* be correlated as whatever the *x*-axis represents changes, but they could not prove it. History will probably prove that this is another example of a common misconception of science and that it confirms certainty on any issue with no errors or uncertainty; this is rarely the case.

As said earlier and as highlighted by the diversity of chapters in this book, the huge majority of scientists working in many different disciplines now do believe that the correlation between CO₂ concentrations and the temperature of the planet is as good as proven, and the temperature will rise from preindustrial levels anywhere between 1.5°C (i.e., 1.5 K) and 5°C (5 K) by the end of the 21st century; the lower end of this range if CO₂ emissions can be stabilized and then reduced, the higher end if no controls are put in place. The language of the fifth Assessment Report (AR5) of the IPCC from 2015 [14] is much stronger than that of the preceding report of 2007 [15], I am sure the language of the Sixth Report, when published, will be even stronger, and these huge documents now have the support of at least 99% of the world's scientists; this was probably not the case for the earlier IPCC reports of the late 20th century. A very small minority of scientists, however, believe genuinely that, while 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 CO₂ concentration is increasing. This has been refuted by world experts—see Chapter 25 in the second edition of *Climate Change*. 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 suggest 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 and second editions because the 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. 2.3. 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 , equal to $k_B T / mg$ (k_B being Boltzmann's constant, T the temperature in K , m the mass of one molecule of the atmosphere (a weighted average of

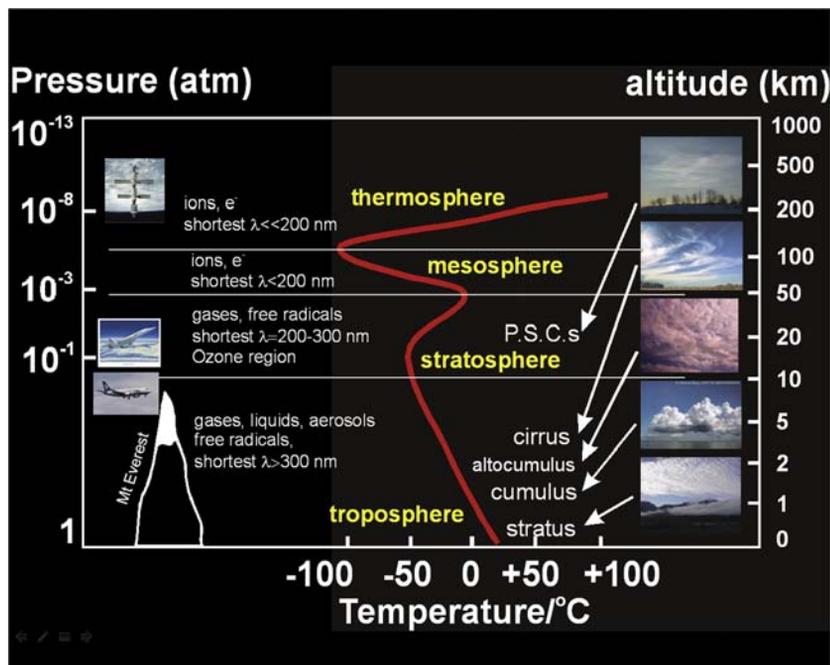


FIGURE 2.3 Different regions of the Earth's atmosphere. About 90% of the gases exist in the troposphere, of which c.99% are N₂ or O₂. Visible photochemistry dominates in the troposphere ($\lambda > \text{c.}390 \text{ nm}$), UV in the stratosphere ($200 < \lambda < \text{c.}390 \text{ nm}$), and vacuum–UV in the mesosphere and thermosphere/ionosphere ($\lambda < 200 \text{ nm}$). Note that 1 atm of pressure is equivalent to $1.01325 \times 10^5 \text{ Pa}$. Note the left-hand y -axis label should read: Pressure/atm and the right-hand y -axis label should read: altitude/km.

N₂ and O₂) in kg, and g the acceleration due to gravity in m/s^2 ; its value is c.8500 m. The temperature drops at a uniform rate through the troposphere ($0 < h < \text{c.}10 \text{ km}$) from c.298 to 210 K, and visible photochemistry (wavelength, $\lambda > \text{c.}390 \text{ nm}$) dominates this region. A temperature inversion occurs over the next 40 km of altitude through the stratosphere ($\text{c.}10 < h < 50 \text{ km}$), 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, and ultraviolet (UV) photochemistry ($200 < \lambda < \text{c.}390 \text{ nm}$) dominates. The mesosphere and ionosphere lie above the stratosphere, where reactions of charged particles (i.e., cations, anions, and free electrons) can be important; vacuum–UV photochemistry ($\lambda < 200 \text{ nm}$), 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 equilibrium since it continually absorbs and emits electromagnetic radiation. As described earlier, 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. This begs an obvious question of why the Earth emits *infrared* radiation which our eyes do

not, of course, see. By energy balance, “energy in” equals “energy out,” and this equality determines what the average temperature of planet Earth 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 per unit frequency versus wavelength for a black body was determined by Planck in the early years of the 20th century and is shown pictorially in Fig. 2.4. Without mathematical detail, two points are relevant. First, the total energy emitted per unit time integrated over all wavelengths is proportional to T^4 . Second, the wavelength of the maximum in the 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 c.500 nm characteristic of $T_{\text{sun}} = 5780 \text{ K}$; this is why we can see the Sun with our eyes! The temperature of planet Earth is a factor of 20 lower, so the Earth’s black body emission curve peaks at a wavelength 20 times longer or c.10 μm . Thus, the Earth emits infrared radiation with a range of wavelengths spanning c.4–50 μm , with the majority being in the range 6–25 μm or c.1700–400 cm^{-1} ; this latter range of wavelengths is sometimes called the *atmospheric window* by climate scientists.

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/m^2), R_e is the radius of the Earth ($6.38 \times 10^6 \text{ m}$), 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 ($5.67 \times 10^{-8} \text{ J/s/m}^2/\text{K}^4$) and $4\pi R_e^2$ is the surface area of the earth. By equating these two terms, at equilibrium the temperature of the Earth, T_e , can therefore be written as:

$$T_e = \left[\frac{F_s(1-A)}{4s} \right]^{1/4} \quad (2.1)$$

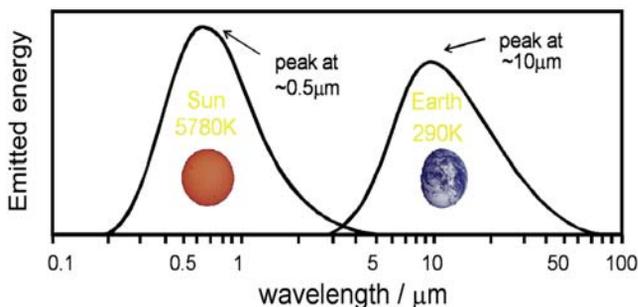


FIGURE 2.4 Black body emission curves from the Sun ($T \sim 5780 \text{ K}$) and the Earth ($T \sim 290 \text{ K}$), showing the operation of Wien’s law that $\lambda_{\max} \propto (1/T)$. The two graphs are not to scale. *With permission, and adapted from A.M. Holloway, R.P. Wayne, Atmospheric Chemistry, RSC Publishing, 2010.*

Using the data earlier, this simple equation yields a value for T_e of c.256 K. Note that, due to the $^{1/4}$ power of the large bracket in Eq. (2.1), any error in the absolute values of F_s , A , and s are significantly reduced or damped out in the error in the value determined for T_e . Mercifully, the average temperature of planet 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 reason why our planet has a hospitable higher average value of c. $+17^\circ\text{C}$ (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 H_2O , CO_2 , O_3 , CH_4 , and N_2O) has trapped this radiation from escaping out of the Earth's atmosphere (just as a garden greenhouse operates), and some is re-radiated back toward the Earth's surface and causes 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 a huge effect, and the dominant primary greenhouse gas is H_2O , *not* CO_2 , O_3 , CH_4 , or N_2O . It is therefore a serious myth to portray *all* aspects of the greenhouse effect as bad news because the reverse is the truth. This fact may explain the confusion there is worldwide about what the greenhouse effect actually is. 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 vapor in the atmosphere, about 3 K is due to CO_2 , and about 1 K is due to all the other primary greenhouse gases. Thus, the major greenhouse gas is H_2O vapor, not CO_2 . It should also never be forgotten that 99% of the Earth's atmosphere is due to N_2 and O_2 , neither absorb infrared radiation (see Section 4), so the greenhouse effect is all due to gases that comprise only c.1% of the atmosphere. Put another way, the atmosphere is very fragile and sensitive to perturbations in concentration of trace species which are greenhouse gases.

It is noted here that the measurement of the surface temperature of planet Earth is very difficult to define, let alone measure. With some justification, many scientists, notably Cheng et al., are querying whether the value for T_{earth} is the most reliable guide to what is happening to our climate, and more-meaningful observables might be the temperature and/or acidity of Earth's oceans [16]. Yet, there has been strong evidence for the presence of greenhouse gases absorbing infrared radiation for many decades, i.e., as long as satellites have been orbiting planet Earth. Fig. 2.5 shows data from the Nimbus 4 satellite circumnavigating the Earth in 1979 at an altitude outside the Earth's atmosphere, although similar observations were reported seven years earlier by Hanel et al. [17]. The infrared emission spectrum in the range 6–25 μm escaping from Earth represents a black body emitter with a temperature of c.290 K, with absorptions (i.e., dips) in the radiance per wavenumber data between 12–17 μm , around 9.6 μm , and $\lambda < 8 \mu\text{m}$. These wavelengths correspond to infrared absorption bands of CO_2 , O_3 , and H_2O , respectively, the three main contributors to the primary greenhouse effect.

Of course, the argument that the primary greenhouse gases have maintained planet Earth at a constant temperature of c.290 K presupposes that their concentrations have remained approximately constant over very long periods of time. As far as we know and indeed confirmed by firm data, this was the case for the primary greenhouse gases, certainly CO_2 , up to the start of the Industrial Revolution, c.1750. However, concentrations of CO_2 , CH_4 , N_2O and, to a lesser extent, O_3 have increased significantly over the following 270 years. It is increases in the concentrations of these and newer anthropogenic (i.e., person-made) gases that absorb infrared radiation strongly in the atmospheric window (where CO_2 , especially,

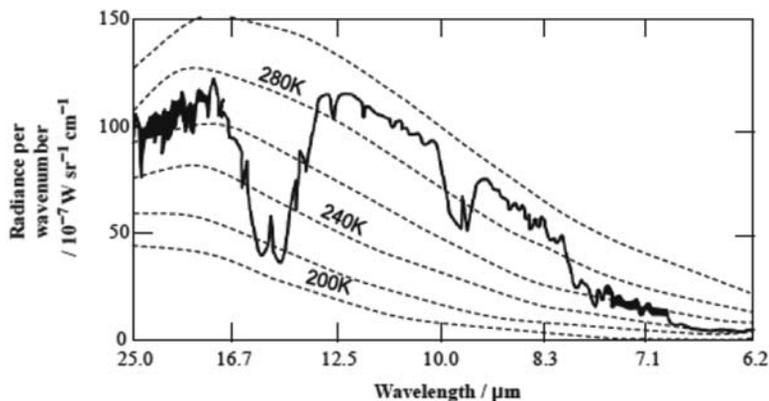


FIGURE 2.5 Infrared emission spectrum as observed in May 1979 by the Nimbus 4 satellite outside the Earth's atmosphere. Absorptions due to CO_2 (between 12 and 17 μm), O_3 (around 9.6 μm), and H_2O ($\lambda < 8 \mu\text{m}$) are shown. With permission from A.M. Holloway, R.P. Wayne, *Atmospheric Chemistry*, RSC Publishing, 2010 with the title and units of the y-axis relabeled; original from R.E. Dickinson, W.C. Clark (eds), *Carbon Dioxide Review* (1982) OUP.

does *not* absorb) that have caused a “secondary” greenhouse effect to occur over this time window, leading to the temperature rises that we are experiencing today. (Although the concentration of H_2O vapor is much higher, it has not changed significantly over the past 270 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 , equals global warming” school of thought. There is no doubt that the concentration of CO_2 in our atmosphere has risen from c.278 ppmv to the current level of 407 ppmv [5] over the past 270 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 1 bar and a temperature of 298 K). It is also not in doubt that the average temperature of planet Earth has risen by 0.9–1.1°C over this same time window (Fig. 2.2). In my opinion, however, what has *not* yet been proven is a cause-and-effect correlation between these two facts, the main problem being that there is insufficient structure or resolution with time in either the CO_2 concentration or the temperature data. 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. 2.6) [18]. 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 precisely with rises in ClO concentration. When presented with these data, 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. 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, a process that is now well understood.

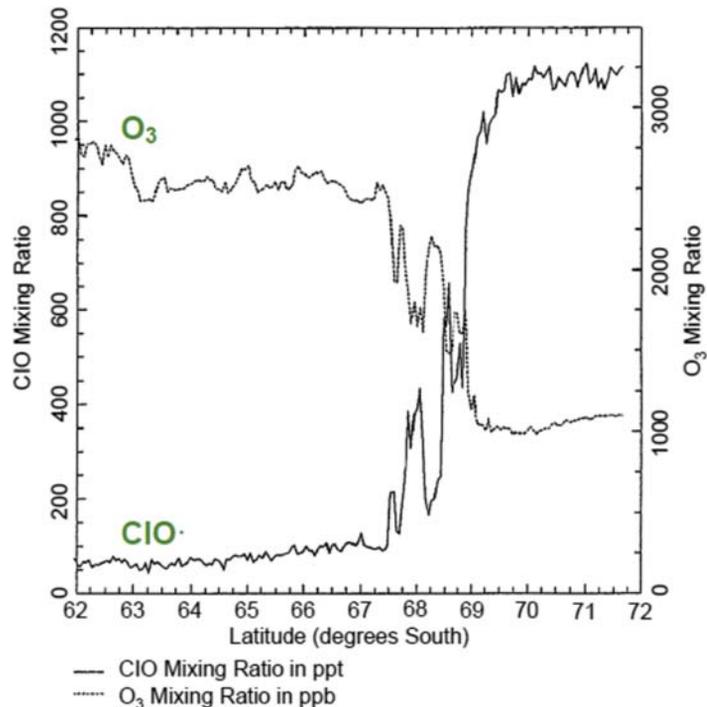


FIGURE 2.6 Anti-correlation between the concentrations of ozone, O_3 , and the chlorine monoxide radical, ClO , in the stratosphere above the Antarctic during their spring season of 1987. 1 ppb is equivalent to one part in 10^9 , 1 ppt to one part in 10^{12} . Note the label on the x -axis should read: latitude/degrees south. With permission from J.G. Anderson, W.H. Brune, M.H. Proffitt, *J. Geophys. Res. D. 94 (1989) 11465*.

This author believes that 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 firm measurements from ice core samples of CO_2 concentrations extrapolated back in time are accurate. Nevertheless, there are two aspects of the “ CO_2 versus T_{earth} ” graph before 1880 AD (i.e., not shown in Fig. 2.2) that remain unanswered by proponents of such a simple theory. First, the data suggest that the temperature of the Earth actually decreased by about $0.15^\circ C$ between 1750 and c.1920 while the CO_2 concentration increased from c.280 to 310 ppmv over this time window. Second, the drop in temperature around 1480 AD, c. $0.25^\circ C$, in the “little ice age” is not mirrored by a similar drop in CO_2 concentration. It is easy to question the accuracy of both the CO_2 concentration and temperature data going back over 500 years. The apparent mirroring of increases in both CO_2 levels and T_{earth} over the recent past 50 years, however, is very striking. The most likely explanation surely is that there may exist 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 “antiphase” and working against each other.

4. The physical 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 6–25 μm . Furthermore, since the primary greenhouse gases of CO_2 , O_3 , and H_2O absorb in the range 12–17 μm (or 830–590 cm^{-1}), 9.6 μm (1040 cm^{-1}), and $\lambda < 8 \mu\text{m}$ ($>1250 \text{cm}^{-1}$), an effective secondary greenhouse gas is one that absorbs infrared radiation strongly *outside* these ranges of wavelengths (or wavenumbers), yet *within* the wider range of 6–25 μm where infrared radiation is present. Indeed, this narrower range of c.8–12 μm (or 1250–830 cm^{-1}) is often where newly discovered anthropogenic greenhouse gases absorb. A molecular vibrational mode is only active in the infrared if the motion of the atoms generates a dipole moment, i.e., $d\mu/dQ \neq 0$, where μ is an instantaneous dipole moment and Q is a displacement coordinate representing the vibration of interest. As said earlier, rather than N_2 and O_2 , there are only trace gases in the atmosphere (Table 2.1) such as CO_2 (0.04%), CH_4 (0.0002%), O_3 ($4 \times 10^{-6}\%$), long-lived chlorofluorocarbons such as CF_2Cl_2 ($5 \times 10^{-8}\%$), and stable

TABLE 2.1 Main constituents of ground-level clean air in the Earth's Atmosphere.

Molecule	Concentration/ x or %		
	x or %	$\mu\text{mol/mol}$ (ppmv) ^a (2018)	$\mu\text{mol/mol}$ (ppmv) ^a (1748)
N_2	0.781 or 78%	780,900	780,900
O_2	0.209 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	10,000
Ar	0.01 or 1%	9,300	9,300
CO_2	4.1×10^{-4} or 0.041%	407.4 ± 0.1^b	278
Ne	1.8×10^{-5} or 0.002%	18	18
CH_4	1.86×10^{-6} or 0.0002%	1.858 ± 0.001^b	0.722
N_2O	3.3×10^{-7} or 0.00003%	0.3309 ± 0.0001^b	0.270
O_3^c	4.0×10^{-8} or 0.000004%	0.040 ± 0.015^b	0.025
All CFCs ^d	8.0×10^{-10} or $8.0 \times 10^{-8}\%$	0.0008 ^b	0
All HFCs and HCCs ^e	1.0×10^{-9} or $1.0 \times 10^{-7}\%$	0.0010 ^b	0
All PFCs ^f	1.0×10^{-10} or $1.0 \times 10^{-8}\%$	0.0001 ^b	0

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

^bData from Table 2.8 of Bull. Amer. Meteor. Soc. 100 (9) (2019) 1–325 [5].

^cThe tropospheric concentration level of O_3 is very difficult to determine because it is poorly mixed. It shows large variation with both region and altitude.

^dChlorofluorocarbons (e.g., CF_2Cl_2 , $\text{CFCl}_2\text{—CF}_2\text{Cl}$).

^eHydrofluorocarbons (e.g., $\text{CH}_2\text{F—CF}_3$), hydrochlorocarbons (e.g., CH_3Cl), and hydrochlorofluorocarbons (e.g., CHClF_2).

^fPerfluorinated molecules (e.g., CF_4 , $\text{CF}_3\text{—CF}_3$, $\text{CF}_3\text{—SF}_5$, SF_6 , NF_3).

fluorinated molecules such as SF₆ ($9 \times 10^{-10}\%$), which contribute to the (secondary) greenhouse effect. Furthermore, the most important trace molecule, CO₂, absorbs via its ν_2 bending vibrational mode at 667 cm^{-1} or $15.0 \text{ }\mu\text{m}$, which is very close to the peak of the Earth's black body curve; the spectroscopic properties of CO₂ have not been kind to the environment! Thus, details of the infrared spectroscopy of gas-phase molecules, in particular at what wavelengths and how strongly a molecule absorbs such radiation, are important properties to determine how effective a trace pollutant will be as a greenhouse gas. This is basic undergraduate physical sciences. Thus, coming to atmospheric science from high-resolution gas-phase spectroscopy, my discipline for the first 20 years of my research career, there is little new in the past c.50 years about the science of greenhouse gases.

The second property of interest is the lifetime of the greenhouse gas in the earth's atmosphere: the longer the lifetime, the greater contribution a greenhouse gas will make to global warming. It is noted that the word *lifetime* can mean different things to different scientists according to their discipline. For a physical scientist, the main physical or chemical processes removing pollutants from the troposphere and stratosphere are reactions with OH free radicals and/or electronically excited oxygen atoms, O*(¹D), and photodissociation in the range 200–300 nm in the stratosphere or 300–500 nm in the troposphere. Thus, the reaction kinetics of greenhouse gases with OH and O*(¹D) and their photochemical properties in the UV/visible will yield important parameters to determine their effectiveness as greenhouse gases. All these data 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 CO₂ whose GWP value is 1. So, a molecule with a large GWP is one with infrared absorption in the atmospheric window where the primary greenhouse gases such as CO₂ 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 2.2. They range between 1 and 23,500, with CO₂ having the lowest GWP value of the eight greenhouse gases shown.

Information in the previous two paragraphs is described in qualitative descriptive 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_0 . It measures the strength of the absorption bands of the greenhouse gas, x , integrated over the infrared black body region of c.400–1700 cm^{-1} . It is a (per molecule) microscopic property and is usually expressed in the unusual units of $\text{W}/\text{m}^2/\text{ppbv}$ (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 270 years from the start of the Industrial Revolution to the current day, an approximate value for the macroscopic radiative forcing in units of W/m^2 is obtained. This simple expression is exact for an anthropogenic greenhouse gas whose concentration has increased from zero to its present-day value (e.g., all CFCs, NF₃, SF₆, CF₃SF₅). For a secondary greenhouse gases whose concentration was not zero in the pre-industrial era, such as CO₂, CH₄, and N₂O, more complicated expressions are needed. These equations, tabulated by Ramaswamy et al. in the IPCC Third Assessment Report of 2001 [19], make the assumption that only *direct* radiative forcing is involved, i.e., no indirect processes (e.g., influences of the concentration of one greenhouse gas on another gas) are involved. Using a different set of simpler parameterized equations, a recent paper by Etminan et al., however, suggests that these earlier expressions may underestimate significantly the

TABLE 2.2 Eight examples of secondary greenhouse gases, and their contributions to global warming.

Greenhouse gas	CO ₂	CH ₄	N ₂ O	CF ₂ Cl ₂ [all CFCs]	O ₃	NF ₃	SF ₆	CF ₃ SF ₅
Concentration (2018)/ μmol/mol or ppmv ^a	407	1.86	0.33	5.0×10^{-4} [8.0×10^{-4}]	c.0.040 ^b	$c.1.0 \times 10^{-6}$	9.6×10^{-6c}	$c.2.0 \times 10^{-7}$
Change in concentration (1748–2018)/ μmol/mol or ppmv	129	1.14	0.06	5.0×10^{-4} [8.0×10^{-4}]	c.0.015	$c.1.0 \times 10^{-6}$	9.6×10^{-6}	$c.2.0 \times 10^{-7}$
Radiative efficiency, $a_o/W/m^2/ppbv^a$	1.37×10^{-5}	3.63×10^{-4}	3.00×10^{-3}	0.32 [0.20–0.32]	3.33×10^{-2}	0.20	0.57	0.59
Total radiative forcing ^{a,d} /W/ m ²	2.04	0.51 ^e	0.20 ^e	0.16 [0.30]	c.0.04 ^f	2.0×10^{-4}	5.5×10^{-3}	1.2×10^{-4}
Contribution from long-lived secondary greenhouse gases, excluding ozone, to overall greenhouse effect/% ^g	66 (58)	16 (15)	6 (6)	5 (5) [10 (9)]	0 (11)	0.006 (0.006)	0.18 (0.16)	0.004 (0.003)
Lifetime, τ/a or years ^h	c.50–200 ⁱ	12.4	121	100 [45–1020]	c.days – weeks ^j	500	3200	800
Global warming potential (100 year projection)	1	28	265	10,200 [4660 –13,900]	– ^k	16,100	23,500	17,400

^aData from State of the Climate 2018 [5], the NOAA annual greenhouse gas index updated Spring 2019 [21], the IPCC AR5 report of 2013 [14], or for NF₃ from Totterdill et al. 2016 [28]. Despite all the detail in this table, the important figure is unchanged over the last c.30 years, that 80%–85% of the total radiative forcing, now 3.10 W/m², is due to two gases, CO₂ and CH₄.

^bGlobal average of 40 ± 20 ppbv [5].

^cM. McGrath, BBC newsfeed, September 13, 2019.

^dDue to change in concentration of long-lived greenhouse gas from the preindustrial era to the present time.

^eMay be an underestimation if indirect processes are allowed for (Etminan et al. [20]).

^fNote an estimated positive radiative forcing of 0.45 W/m² in the troposphere is partially canceled by a negative forcing of 0.05 W/m² in the stratosphere [5,14].

^gAssumes the latest value from 2018 for the total radiative forcing of long-lived greenhouse gases, 3.10 W/m² [21]. The values in brackets show the percentage contributions when the estimated radiative forcing for ozone, 0.40 W/m², is included in the value for the total radiative forcing.

^hAssumes a single-exponential decay for removal of greenhouse gas from the atmosphere.

ⁱCO₂ does not show a single-exponential decay (Shine et al. [22]).

^jO₃ is poorly mixed in the troposphere, so a single value for the lifetime is difficult to estimate. It is removed by the reaction OH + O₃ → HO₂ + O₂. Its concentration shows large variations both with region and altitude.

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

radiative forcing of CH₄ and possibly N₂O, the former by as much as 25% [20]. That all said, the most recent figures give a total radiative forcing for long-lived greenhouse gases, but excluding ozone (see Table 2.2), of 3.10 W/m² [21]; the values in the IPCC fifth, fourth, and third Assessment Reports were 2.83, 2.63, and 2.43 W/m², respectively. This steady increase in total radiative forcing of long-lived secondary greenhouse gases over the past 20 years cannot be disputed. In each of these four cases, the combined contribution from CO₂ and CH₄ is 80%–85% of the total, and this percentage has not changed; the NOAA Spring 2019 compilation states that the CO₂ radiative forcing is 2.04 W/m² and CH₄ is 0.51 W/m², making 82% of the total of 3.10 W/m² [21]. Effectively, the radiative forcing value of a greenhouse gas gives a current-day estimate of how serious a greenhouse gas will be to the environment *in the future* but uses concentration data *from the past*. Note that a pollutant, whose concentration has not changed over this long time window, such as H₂O, will have a macroscopic radiative forcing of zero.

The overall effect of one molecule of pollutant on the Earth's climate is also 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 *in the future*, t , usually 100 years, relative to the time-integrated radiative forcing of a pulse emission of an equal mass of CO₂:

$$\text{GWP}_x(t) = \frac{\int_0^t A_x(t) \cdot dt}{\int_0^t A_{\text{CO}_2}(t) \cdot dt} \quad (2.2)$$

The GWP value therefore informs how important one molecule of pollutant x is to global warming via the greenhouse effect compared with one molecule of CO₂, which is defined to have a GWP value of unity. It is an attempt to project how serious the presence of a long-lived greenhouse gas will be in the atmosphere. (When the media state, therefore, that CH₄ is 28 times as serious as CO₂ for global warming, what they are saying is that the GWP₁₀₀ value of CH₄ is 28; one molecule of CH₄ is expected to cause 28 times as much “damage” as one molecule of CO₂ over the next 100 years.) For most greenhouse gases, the radiative forcing following an emission at $t = 0$ takes a simple exponential form:

$$A_x(t) = A_{o,x} \exp(-t / \tau_x) \quad (2.3)$$

where τ_x is the lifetime for removal of species x from the atmosphere. For CO₂, a single-exponential decay is not appropriate because the lifetime ranges from 50 to 200 years, dependent on latitude and longitude. Eq. (2.3) is then modified to:

$$A_{\text{CO}_2}(t) = A_{o,\text{CO}_2} \left[b_0 + \sum_i b_i \exp(-t / \tau_i) \right] \quad (2.4)$$

where the response function, the large bracket in the right-hand side of Eq. (2.4), is derived from more complete carbon cycles. Values for b_i ($i = 0-4$) and τ_i ($i = 1-4$) have been given by Shine et al. [22]. The values of radiative forcing, A_o , in Eqs. (2.2)–(2.4) have units of W/m²/kg, and it is therefore given a different symbol to the microscopic radiative efficiency, a_o , with alternative units of W/m²/ppbv. The time integral of the large bracket in Eq. (2.4), defined

K_{CO_2} , has dimensions of time and takes values of 13.4 and 45.7 years for a time period of 20 and 100 years, 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 parameterize Eq. (2.2) to give an analytical expression for the GWP of x over a time period t [23]:

$$\frac{\text{GWP}_x(t)}{\text{GWP}_{\text{CO}_2}(t)} = \frac{MW_{\text{CO}_2}}{MW_x} \cdot \frac{a_{0,x}}{a_{0,\text{CO}_2}} \cdot \frac{\tau_x}{K_{\text{CO}_2}} \cdot \left[1 - \exp\left(\frac{-t}{\tau_x}\right) \right] \quad (2.5)$$

In this simple form, the GWP only incorporates values for the radiative efficiency of greenhouse gases x and CO_2 , $a_{0,x}$ and a_{0,CO_2} ; the molecular weights of x and CO_2 ; the lifetime of x in the atmosphere, τ_x ; the time period into the future over which the effect of the pollutant is determined; and the constant K_{CO_2} , a measure of the non-single value of the lifetime of CO_2 , which can be calculated for any value of t [22]. 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 some pollutants (e.g., the rapid rise per annum in SF_6 concentration over the past decade) does not contribute directly to the GWP value. This and other factors have caused some criticism by Shine et al. of the use of GWPs in policy formulation [22].

5. Interpretation of data for the properties of greenhouse gases

Data for eight secondary greenhouse gases are shown in Table 2.2. (Although H_2O vapor is the most abundant greenhouse gas in the atmosphere, it is neither long-lived nor well mixed: concentrations range from 0% to 3%, i.e., 0–30,000 ppmv, over different parts of the Earth, and its average lifetime is only a few days. Since its average global concentration has not changed significantly since the middle of the 18th century, it has zero radiative forcing and is not included.) CO_2 , CH_4 , N_2O , and O_3 are naturally occurring greenhouse gases whose concentrations ideally would have remained constant at pre-Industrial Revolution levels. The a_0 values of CH_4 , N_2O , and O_3 are significantly greater than that of CO_2 , but their concentrations are two to four orders of magnitude lower. The CH_4 concentration, although small, has increased by 158% since pre-Industrial times, a much greater percentage increase than even CO_2 , 47%; CH_4 is the second most important greenhouse gas, and its current radiative forcing is 25% that of CO_2 [21]. The concentration of N_2O has increased by 23% over this same time period, and it has the third highest radiative forcing of all naturally occurring greenhouse gases. Dichlorofluoromethane, CF_2Cl_2 or CFC-12, has the highest concentration of all chlorofluorocarbons. These person-made, anthropogenic chemicals have grown in concentration from zero in pre-Industrial times to a current total concentration of 804 pptv or 0.804 ppbv [5]; 1 ppbv is equivalent to a number density of 2.46×10^{10} molecules cm^{-3} at a pressure of 1 bar and a temperature of 298 K. Their concentrations are now decreasing, but slowly because of their long atmospheric lifetimes, due to the 1987 Montreal and later International Protocols introduced to halt destruction of stratospheric ozone. SF_6 and CF_3SF_5 are two long-lived perfluorinated molecules with currently very low concentration levels but high annual percentage increases, and exceptionally long lifetimes in the atmosphere.

They have very high a_0 and GWP values, essentially because of their large number of strong infrared-active vibrational modes in the atmospheric window and their long lifetimes. NF_3 is probably the latest secondary greenhouse gas recorded in such tables. It was not included in the Kyoto Protocol listing of greenhouse gases for long-term monitoring [24], but there is now agreement from IPCC reports since 1997 that it should be included in future protocols.

CO_2 and CH_4 have the lowest GWP values of all the greenhouse gases listed. It begs the obvious question; why is such concern expressed 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 contribution of a pollutant to the greenhouse effect, present *and* future, qualitatively involves a convolution of its concentration with its GWP value. Thus, CO_2 and CH_4 currently contribute most to the greenhouse effect (third bottom row of Table 2.2) mainly because of their large change in atmospheric concentration since the Industrial Revolution. Note, however, that the a_0 and GWP values, a per *molecule* microscopic property, of both gases are relatively low. By contrast, CF_3SF_5 is a perfluorocarbon molecule with the highest a_0 value of any known greenhouse gas (earning it the title “super” greenhouse gas [23,25]), 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 as first noted by Sturges et al. [26], the variations of concentration levels of SF_6 and CF_3SF_5 in the past 50 years have tracked each other closely. Their GWP values are high, SF_6 being slightly higher because its atmospheric lifetime, c.3200 years [27], is about four times greater than that of CF_3SF_5 . However, the contribution of these two molecules, especially CF_3SF_5 , to the overall greenhouse effect is still small because their atmospheric concentrations, despite rising rapidly at the rate of c.6%–7% per annum, are still very low, at the level of parts per 10^{12} (trillion) by volume.

With one exception of the total radiative forcing of secondary greenhouse gases (the sum of the individual components in row 4 of the table), what is perhaps most revealing about Table 2.2 is that nothing of real significance to the climate debate has changed in the past c.50 years. The data of Tables 2.1 and 2.2 are mostly taken from the IPCC AR5 from 2013 [14] and two subsequent updates, the NOAA annual greenhouse gas index of Spring 2019 [21] and the State of the Climate 2018 report [5]. Some of the finer details (e.g., accuracy of a_0 values and lifetimes of greenhouse gases) plus improved data for photodissociation cross sections of greenhouse gases as a function of both wavelength and temperature have improved hugely. A few new long-lived gases, such as NF_3 and perfluorotributylamine, $\text{N}(\text{C}_4\text{F}_9)_3$, have also been discovered in the atmosphere [28,29]. The *important* figure, however, has not changed; 80%–85% of the total radiative forcing is due to two gases only, CO_2 and CH_4 , with the former's contribution remaining three to four times that of the latter's. It is accepted that 15%–20% is due to other long-lived species, and keep atmospheric scientists busy with requests for money to study their properties! But it is surely imperative that the public concentrates on what really counts, i.e., CO_2 and CH_4 . Furthermore, the total radiative forcing of secondary greenhouse gases is increasing fairly consistently (1.17 W/m^2 in 1960, 1.48 W/m^2 in 1970, 1.91 W/m^2 in 1980, and 2.45 W/m^2 in 1990 [the IPCC First Assessment Report]). It then increased to 2.45 W/m^2 in 1995 (the IPCC Second Assessment Report), $2.43 \pm 0.24 \text{ W}/\text{m}^2$ in the Third Assessment Report of 1998 [19], $2.63 \pm 0.25 \text{ W}/\text{m}^2$ in the Fourth Assessment Report of 2007 [15], $2.83 \pm 0.29 \text{ W}/\text{m}^2$ in the Fifth Assessment Report

of 2013 [14], and now 3.10 W/m^2 from the NOAA Spring 2019 report [21]. In all these reports, the radiative forcing budget is dominated by CO_2 and CH_4 emissions.

Furthermore, if we concentrate on CO_2 , its increasing concentration in the atmosphere shows no sign of slowing down, with the current value now definitively higher than the emotive level of 400 ppmv. There is nothing special about this number, *per se*, but the general view of climate scientists has always been that if this value gets close to 550 ppmv the Earth's atmosphere will likely 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*; it is caused by positive feedback whereby an increasing temperature causes an increasing concentration of water vapor in the atmosphere, which causes an ever-increasing temperature rise through the primary greenhouse effect, and the cycle repeats. We should also note that the 550 ppmv figure is decreasing as the modelling improves, with much depending on how the word "likely" is interpreted. However, modellers also have predicted that if the CO_2 concentrations can be stabilized at the current levels of c.400 ppmv by 2020, then reduced to less than half of 1990 levels by 2050, and continue cutting them thereafter, then the rise in temperature from preindustrial times to the end of the 21st century may be limited to around 2°C (or K). Fig. 2.2 makes it clear that we are already 1.1°C there. The predictions from the UN conference in Incheon, South Korea, in October 2018, however, are that this is not enough, and the world should be aiming for an increase of only 1.5°C or K. Many cities, at least in the United Kingdom, and countries have now committed themselves in the past 12 months to become *net zero carbon* within 30 years by 2050, some even quicker; Birmingham in the UK where I live has a target of 2030. It remains to be seen whether this incredibly demanding target, however the phrase *net zero carbon* is defined, can be achieved.

Some general comments on *very* long-lived, i.e., lifetimes >100 years, secondary greenhouse gases now seem appropriate. 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*" [30]. Their example to justify this policy was CFC 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 from the 1960s showed that these molecules with lifetimes of several hundreds of years were unfortunately having an unforeseen deleterious effect on the ozone layer in the stratosphere [31] and ultimately led to the Montreal Protocol of 1987 and the gradual elimination of these molecules from production [32]. 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. Indeed, the latest predictions are that the ozone layer in the stratosphere will recover to its levels of around 1950 within the next 50–100 years, and the problem created by these molecules will have been reversed [33]. Scientists now believe that the issue of carbon dioxide concentrations and global temperature is the modern-day equivalent, but a much more difficult problem to solve.

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, I believe, population levels on planet Earth. The *microscopic*

properties of these compounds, however, are controlled by factors that undergraduates worldwide learn about in science degree courses: infrared spectroscopy, reaction kinetics, and UV/VIS absorption cross sections. I contend that the scientific case is now so strong and accepted by 99%+ of the world's scientists that, as a population of c.7.7 billion people, 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, the extrapolation of the CO₂/temperature of Planet earth versus time stretching back nearly 1000 years, are unexplained (see [Section 3](#)) [34]. But this should not blinker us to the major environmental issue that needs to be addressed.

6. What has changed in the past decade?

6.1 Have public perceptions of greenhouse gases changed?

This is a difficult question to answer, and any response is subjective. But my 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 UN convention in Copenhagen, Denmark, in 2009 attracted huge publicity worldwide, even if it did not result in much tangible action [35]. An overriding impression from television, alas, remains that of President Obama jetting into the country in Air Force 1 and jetting out 24 h later, rather missing the point that air travel is a serious component of carbon emissions. The power of the Internet increases exponentially with time, and this and social media are now major components of attracting multimillion petitions beseeching national governments to act. Unfortunately, bad publicity can halt any positive momentum built-up. Reports at the same time that the University of East Anglia in the United Kingdom had suppressed emails to international colleagues suggesting that the issues around global warming were not as serious as reported and were hugely damaging. Many people now believe that “*Climategate*” was a major contributor to the apparent failure of the Copenhagen Summit.

At a national level, Europe is leading the way and the United Kingdom 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 CO₂ emissions by 2020 to less than 74% of the level in 1990 [36]. In the last weeks of Prime Minister May's tenure in July 2019, this target was strengthened and the United Kingdom now has an official target to be *net carbon neutral* by 2050. Many pressure groups, however, think this is not quick enough, and there are different definitions of what *net carbon neutral* actually means. Such targets are commendable, but nobody says what will happen if this 2050 target is not met. In 2014, the European Union, of which the United Kingdom is (still just!) 1 of 27 members, committed to reduce CO₂ 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 [37]. 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 quoting of statistics in such percentage terms can seem rather bland and is at times not very useful. Furthermore, following Allen et al. in their major contribution to the IPCC

Assessment Report 3 of 2001 [38], people are now talking much more about amounts of carbon-based fossil fuels in the atmosphere rather than concentrations of greenhouse gases with their arcane units of parts per million (or billion or trillion) by volume. The UK and EU commitments in the previous paragraph can therefore usefully be expressed differently in units of *metric tons (T) of CO₂ emitted per person per year*, again not exactly the most SI of units! But it is convenient to use because the absolute values are finite and involve no large powers of 10, and hopefully therefore more understandable by the public. That said, averaging CO₂ emissions of any country to a figure *per person* can be misleading because it includes the very young, very old, and infirm who have no power to influence their contribution. With that caveat, Fig. 2.7 shows graphically where the CO₂ was emitted in 2018 in different countries of the world, and Fig. 2.8 shows how much CO₂ was emitted *per person per year* from 1960 to 2018. Data from Fig. 2.8 are tabulated for some different countries in Table 2.3. In these units, the UK average at the moment is 5.6, the US average is 16.6, China average is 7.0, India average is 2.0, and the global average is 4.8. Nearly every country in the industrialized west has reduced their figure in the past 30 years since the first IPCC Assessment Report (AR1) was published, but the target for 2100 *for everybody* is below 1; this is the figure that modellers predict is needed to avoid the worst effects of climate change in the next 80 years, i.e., to limit the increase in global temperatures to 1.5°C (or K) above that in pre-Industrial times. By any standards, these are huge changes. In 2014, President Obama finally committed the United States to a major reduction of greenhouse gases, but these policies were reversed by his successor in January 2017. The two largest populations in

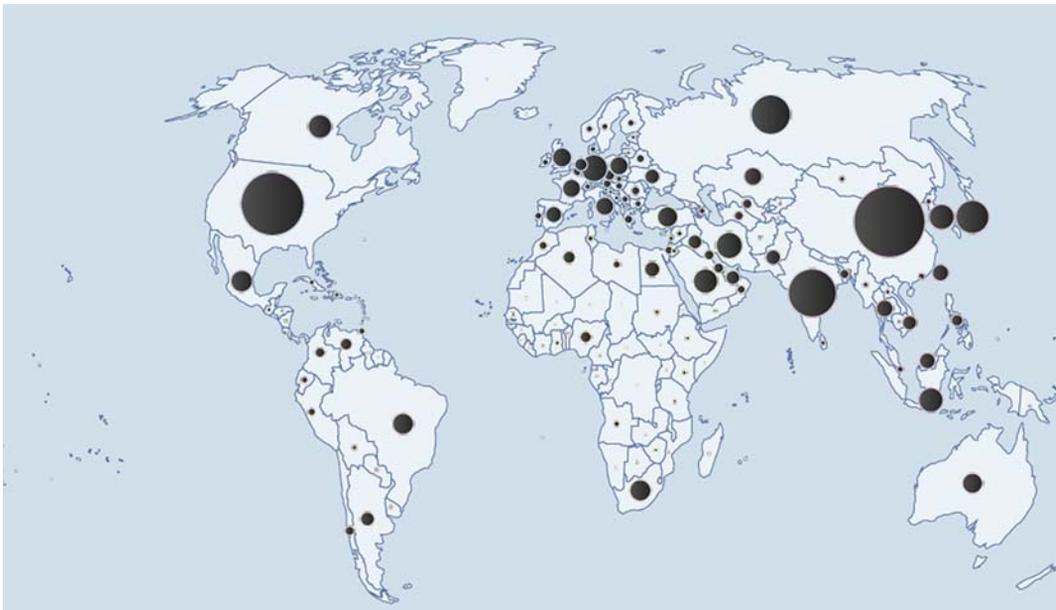


FIGURE 2.7 Emission of CO₂ for calendar year 2018; global emission was 3.6573×10^{10} T or 36.573 GT. The size of the black circle is proportional to the amount of CO₂ emitted by each country. *With permission, data from <http://www.globalcarbonatlas.org/en/CO2-emissions>.*

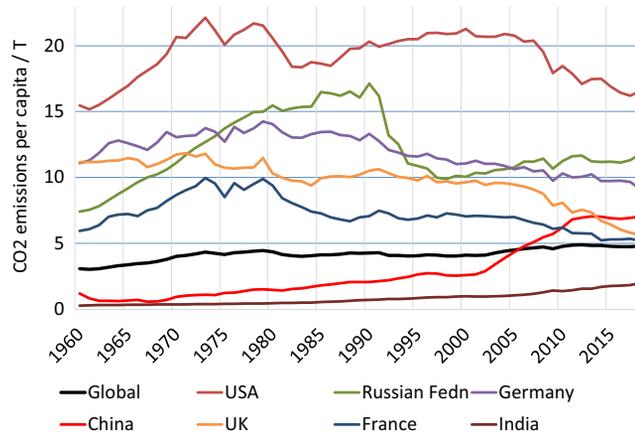


FIGURE 2.8 Global emission levels of CO₂ per capita (in T), and from seven countries over the period 1960 to 2018. The world population has increased by 150% over this time period, but global emissions have risen more steeply from 9.3 to 36.6 GT (i.e., by 288%). Emissions per capita have therefore increased continuously from 3.1 to 4.8 T. With permission, CO₂ emissions from <http://www.globalcarbonatlas.org/en/CO2-emissions>. With permission, population levels from <https://www.worldometers.info/world-population/world-population-by-year/>.

TABLE 2.3 Amount of carbon dioxide individuals can emit if the increase in the Earth's temperature is to be limited to 1.5°C above the pre-Industrial era by the year 2100.

	Population/billion (2018)	(1960)/T	(1990)/T	(2018)/T	(2100)/T
Planet Earth	7.63	3.1	4.3	4.8	<1
China	1.43	1.2	2.1	7.0	<1
India	1.35	0.3	0.7	2.0	<1
Africa	1.28	~1	~1	~1	<1
EU average	0.51	~8	~9	~7	<1
United Kingdom	0.07	11.2	10.5	5.6	<1
Poland	0.04	6.8	9.9	9.1	<1
France	0.06	5.9	7.1	5.2	<1
Germany	0.08	11.1	13.3	9.1	<1
United States	0.33	15.5	20.3	16.6	<1
USSR Federation	0.29	7.4	17.1	11.7	<1

Historical data are given for the years 1960, 1990, and 2018, the units are metric tons (T) per person per year where 1 T equals 1000 kg. In 2018, the total world emission of CO₂ was 36.573 GT (or 3.6573×10^{10} T), and the world population was 7.63 billion. All values of per capita emissions are approximated to one decimal point. With the exceptions of China and India, per capita emissions started to reduce in all countries following the first IPCC Assessment Report 1 published in 1990.

Data from <http://www.globalcarbonatlas.org/en/CO2-emissions> and <https://www.worldometers.info/world-population/world-population-by-year>.

the world, China and India, have yet to declare any binding targets, their current levels are at the low end, but their per capita emissions have increased significantly over the past 30 years (Table 2.3). This is unfortunate, because the overriding reaction from Europeans effectively says: “*what difference will anything I do as an individual make to this global problem, when China’s total emissions [especially] are so huge compared to those of European countries?*” I believe that a binding target set by these countries would help Europeans believe that Asia was taking the issue seriously and might help individuals in Europe do more themselves. One should also not forget that it is the industrialized first-world countries in the west, mostly Europe and North America, that have, in the main, created the current problem.

But perhaps most encouraging for the future, the mantra of the developed world for the past 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 past 5–10 years, 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 which 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 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 necessarily, challenge the criteria on which countries have based their policies and lifestyles in the past 50+ years.

6.2 What should we do?

An outpouring of guilt will get us nowhere, and there are now many examples of excellent practice emerging from individuals, certainly in the United Kingdom. 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 probably electric cars will be the standard in only 10 years time), and the increase in bicycling and walking by healthy people are just four examples. But one must be honest; these examples scratch at the scale of the problem, and only the educated “converted” are taking these actions. National policies must be imposed, and although it goes against the instincts of all politicians to “*tell people how to live their lives,*” that 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, global solutions are needed and the normal “rules” of economics cannot apply. So attempts to trade carbon, i.e., the “transfer” through payment of emissions to other countries, cannot possibly succeed. It amounts to rich countries buying permission to continue polluting the atmosphere and is therefore a short-term solution of dubious morality to a long-term global problem. It is doomed to fail.

If the atmosphere is to be decarbonized, in simple terms this becomes an issue of *supply* and *demand*. Certainly in the United Kingdom, much of the debate to date has concentrated on the *supply* side; what is the best low-carbon way to provide the energy needed for its growing population? Others in this book may write with more knowledge about possible ways to (1) change our energy policy to become less reliant on the burning of conventional

fossil fuels, (2) trap emissions of greenhouse gases, and possibly (3) engage in geo-engineering to reduce incoming radiation from the Sun as a means to control our increasing temperature. Under category (1) falls a renaissance in nuclear energy, and possibly the huge expansion of fracking, the release of shale gas reserves from deep within rocks. Whenever the former policy seems to be gaining favor, a serious accident, such as that at Fukushima in northern Japan in 2011, can set the clock back by decades. Germany changed almost immediately to a nuclear-free energy policy, and the United Kingdom has not yet committed to a big expansion in this technology that seemed likely in the decade before 2011. (It is ironic that while Green parties have considerable political influence in Germany, their emissions of CO₂ have always exceeded the EU average (Table 2.3) because, especially post-2011, they rely on carbon-burning coal for much of their energy.) The risks involved in following the latter policy of fracking are significant, if only because of the large increases in methane gas in the atmosphere that are likely to happen; nothing can change the science that one molecule of CH₄ will cause 28 times as much damage to the world's climate as one molecule of CO₂ over the next 100 years. The potential benefits of nuclear energy, however, are considerable if only because it is a carbon-free technology, but the problems of nuclear waste remain still effectively unsolved. Categories (2) and (3) can simply be interpreted as possible solutions to a problem that has been allowed to develop unchecked.

Much less comment has been made on the *demand* side and how lifestyles could adapt to mitigate the worst excesses of the climate emergency. This is understandable because personal choices will become involved, but this situation is changing rapidly with the increasing influence of Thunberg and Extinction Rebellion. Surely it is also sensible to follow the advice of Ravishankara and Lovejoy [30] and reduce the amounts of emissions from damaging greenhouse gases in the atmosphere in the first place. In simple language, 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 we are serious about this issue, and (3) incredibly complex issues that must be addressed, probably by the United Nations. For individuals in the United Kingdom, they can be summarized easily: fly less, drive cars less and walk/bike more, insulate your home properly, eat less meat, and have fewer children.

6.2.1 *Easy to implement*

Nobody can turn back the clock on scientific progress. The challenge therefore to reduce 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 past 200 years. That said, in the author's and many other opinions, some solutions are obvious. An excellent book, *Sustainable Energy—without the hot air* written by MacKay in 2009, and available free on the Internet, shows where the UK emissions come from at a personal level [39]. The figures are now over 10 years out of date and, very sadly, the author died at a young age in 2016 so they have not been updated. However, in 2009, MacKay believed that, on average, every person used 125 kWh of energy per day. Any suggestions for action must be country specific. In the United Kingdom, he estimated that wearing more clothes and turning down thermostats by a few degrees both at home and work might reduce this figure by about 20 such units; stopping flying might cause a reduction of 35; 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 defined, might 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 enshrined in law, with exceptions built in for vulnerable groups such as the young, the old, the disabled, and the infirm.

It is appropriate to make some comments on the two different units now commonly used in scientific papers or books: emission of CO₂ in tonnes (T) per person per year, where 1 T equals 1000 kg, and energy usage in kilowatt hours (kWh) per person per day. They measure different aspects of the emerging climate emergency, but essentially both need to have low values. There is no single interconversion factor between the two because it depends how the energy is produced, but roughly 1 T of CO₂ emission is equivalent to using between 3000 and 5000 kWh of energy; the former figure applies if burning hard coal and the latter if burning natural gas is the source of energy [40]. MacKay's figure in 2009 of 125 kWh energy per day is therefore equivalent to c.15 or 9 T per year of CO₂ emission if burning coal or gas is the main energy source. This agrees with data from the World Carbon Atlas (Fig. 2.8) that the UK average in that year was 7.9 T per person per year, given that some people have always been incredibly economic with energy usage.

It is suggested that the working temperature for employees in offices often considerably exceeds the guideline of 16°C minimum by several degrees; this minimum should become the norm. MacKay effectively also asks whether we must live only in shirt sleeves for our waking hours [39]! Could European health and safety legislation be modified to reduce unnecessary packaging on much food and “excess clutter”? The UK legislation of 1994 that allowed for Sunday trading for 6 h per day could be reversed; Sunday closing remains the law in Switzerland, and it is probably the richest European country. Demand for domestic air travel within a small country such as the United Kingdom could be priced out of the market; with a corresponding investment, then there could be increase in rail travel. (Hopefully this will happen when the High Speed 2 [and HS3, HS4 ...] train routes from London to the north of England/Scotland are completed.) One could ask further whether much long-distance air travel for business meetings is really necessary, and whether technology can assist; the Skype principle for 1:1 conversations has already been extended so that now more than two people can easily meet remotely. Could academia set an example, with remote conferences, especially talks by plenary lecturers, becoming more common? Many other simple-to-enact 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.

Use of private cars in the United Kingdom is an interesting example of how people fixate on one particular issue but ignore the bigger picture. At the start of this century, all the talk focused on carbon reduction, and diesel became “in” and petrol became “out.” Fifteen years later, the focus changed to quality of air in cities, so suddenly diesel has also become “out.” In 20 years' time, all new petrol and diesel cars will have been phased out, the electric car revolution is just starting, but already there is concern about the load on the grid as all cars regularly need re-charging. Nobody seems to have said the obvious that perhaps the United Kingdom should somehow rid itself of its love affair with the motor car, and we drive less. If the annual usage of an average car in the United Kingdom was reduced from

10,000 to 5,000 miles, the saving in CO₂ emissions is estimated to be about 2 T. If car usage were to decrease significantly, then perhaps employment patterns could change. Is it sensible for a couple to work midway between two places of employment, with one person driving, say, 30 miles in one direction, the other driving 30 miles in the opposite direction five days a week? Today, this is common practice. Perhaps a huge rollout for office-based personnel of working certain days a week from home, helped by technology and significant government financial help, could be the way forward. Perhaps, there could be financial incentives to work and live a smaller distance apart than is often the case currently in the United Kingdom?

The author accepts that, at the age of 65, it is easy to make such suggestions. Would he write the same if he were now 25 years old? Probably not. For example, is it realistic in 2019 to ask every person in the United Kingdom to stop flying? The answer has to be “No.” Furthermore, flying to other countries over the past 70+ years has bought enormous benefits to human understanding of other cultures and has made the world a better place. All this chapter can do is give data, make suggestions, and leave individuals to make their choices.¹

6.2.2 Moderately difficult to implement

Individuals can only do so much. At this point, national governments should move in, accepting that many of their policies might be deeply controversial, cost money, and lose votes. I highlight two such issues. The unit of carbon emission that everyone would understand is the cost to their pocket. All developed countries could therefore move to a system of taxation whereby the principle of “*polluter pays*” becomes dominant. A universal carbon credit card could then result where money is charged for excess use of domestic energy, road usage, and certainly air travel. This idea was mooted for road travel by the UK government 15 years ago but was quickly dropped when public reaction, to say the very least, was negative. Prime Minister Blair infamously also then said that climate change would not be solved by everyone stopping flying; he was surely correct in saying it was inconceivable for all air travel to cease, but it might have helped if he had suggested that individuals review the necessity of their air travel. Canada has mooted a carbon tax for the last 10+ years but nothing so far is implemented. If one developed country implemented such a policy, others would surely follow rapidly, but nobody wants to be first. Now that climate issues are top of the political agenda in almost all developed countries, this could change rapidly.

A different issue concerns food production, *what* we eat, and *where* the food comes from. The more anyone looks at the food supply chain, the more baffled s/he becomes. For example, *why* does food often travel such huge distances between source and consumption? Is it necessary? For the past 65 years since the end of rationing in the United Kingdom, the principle that the customer has a paramount right to food at the cheapest price *and at any time of year* has swept aside environmental consequences: excess use of fossil fuels for food transportation and preservation. We could then address *what* we eat. Cattle use much limited land for grazing, and there is a strong argument that we should reduce meat consumption, if not become vegetarians of whatever strictness; a policy effectively advocated by MacKay, thereby also reducing methane emissions, see the following. The population then may reduce its dependency on cattle as a source of food, *including* dairy products.

¹This chapter was written before the COVID-19 pandemic had started.

For the past few decades, CO₂ and CH₄ together contribute c.80%–85% of the total radiative forcing of long-lived secondary greenhouse gases [21], but it is naive to say that reduction of CO₂ levels alone will be the complete solution. In simple terms, atmospheric CO₂ levels correlate loosely with lifestyle of the population, and with serious effort, especially in the developed world, huge reductions are possible; examples are given earlier in this chapter. In the author's opinion, however, CH₄ poses just as serious a threat as CO₂ simply because its level, while smaller than that of CO₂, will be much harder to reduce. While it remains unclear why the radiative forcing of methane, currently between 0.5 and 0.6 W/m² depending on the method used for its determination [20,21], has shown little change over the past two decades, a major component of its emissions correlates *strongly* with the number of animal livestock, which itself is dependent on the world population. Note also that it is due to the potential for huge increases in methane emissions following shale-gas fracking in the United Kingdom that this technology should be rejected here.

These two issues of carbon taxing and food apply to all developed countries, and different places will implement different means to tackle them. On the author's scale, however, these issues are *moderately difficult* to solve, but such painful projects must be addressed if planet Earth is going to be a pleasant place to live for the majority of its population.

6.2.3 *Incredibly difficult to implement*

The population of the planet dominates this category, and the figures are stark [41]. Fifty years ago, the population was 3.6 billion (3.6×10^9); today, it is 7.7 billion and may rise to c.11 billion by the year 2100, with the large majority of growth expected in sub-Saharan Africa and Asia. While 75% of the world's population currently live in these two continents, that figure is predicted to grow to 82% by the end of the century. Conversely, the population of Europe, currently c.0.5 billion, is predicted to decrease both in absolute terms and as a percentage of world population. This is an emotive and complex issue, with a range of views whether world population is or is not an issue in the climate argument. Both sides of this argument are probably correct. The per capita CO₂ emission and usage of energy is vastly smaller in many third world countries, especially Africa, compared with the first world (Table 2.3), and therefore, it may seem hypocritical for the latter to criticise population levels in the former; they are focusing on the wrong problem [42]. Up to a point, this is true, and a carbon tax (\$6.2.2) over time should reduce carbon usage in the first world. But the fact remains that, once born, every person will need housing and feeding for their lifetime, as repeatedly pointed out by many high-profile individuals (e.g., David Attenborough) and pressure groups [43]. A global scarcity of water will also become increasingly serious if population levels grow too much; South Africa has become the first major country to face just this problem in the past year. For these reasons, this author believes that world population *is* an important issue in the climate debate.

If this contentious point can be accepted, population control on a worldwide scale has to be discussed openly and the subject cannot be avoided if carbon emissions are to be controlled. This is one policy area that even the most outspoken politician is reluctant to discuss. The current message from the West is mixed. First-world countries have always believed in the absolute right of individuals to make their choice of family size independent of the state, but their governments could exert influence by limiting financial access to the state for families above a certain size. That said, family sizes in the West decreased

significantly once contraception became freely available in the 1960s, but ironically no government wants population levels to drop too much because of loss of revenue from taxation. To take four current examples, Japan is worried simply about how few children are being born to provide sufficient tax revenues in their working years, China is also becoming increasingly concerned about who will look after their elderly, while Australia and Denmark (to name but two) are almost bribing couples to have more children. (China has not gone that far but is now encouraging its huge population to have more children, a complete U-turn on its one-child-per-family policy from 1980 to 2016.) Conversely, the leaders of the Catholic Church, comprising c.15% of the world's population and much of it in poorer countries, will not discuss the matter in public, believing in the absolute sanctity of life and refusal to accept any form of contraception. The situation is a mess, but any discussions must surely start with sub-Saharan Africa and Asia because projected increases here, especially in the former, are the greatest.

Controlling the increase of, let alone reducing, world population levels is a huge policy area that calls for intergovernment agreements at all levels. It calls for patience and understanding of others' lifestyles in different continents, a *"one size fits all"* policy will not work, and compromises from currently held positions will be needed. For all its faults and decreasing respect with which it is viewed, the United Nations is surely the only global organization that could lead on this issue; it could become their major policy directive for the next few decades. World leadership is surely needed to bring about this step change in public perception and subsequent action.

Acknowledgments

I thank many friends and colleagues over many years for illuminating discussions on this difficult issue, but especially Dr Harriet Martin of the Quaker Living Witness (<http://www.livingwitness.org.uk>).

References

- [1] R.P. Tuckett, *Climate Change: Observed Impacts on Planet Earth* (Chapter 24), second ed., Elsevier, 2015. ISBN: 978-0-444-63524-2.
- [2] L. Cheng, K.E. Trenberth, J. Fasullo, J. Abraham, T.P. Boyer, K. von Schuckmann, (2017) <https://eos.org/opinions/taking-the-pulse-of-the-planet>.
- [3] B. Meyssignac, et al., *Front. Mar. Sci.* (2019), <https://doi.org/10.3389/fmars.2019.00432>.
- [4] H.O. Pörtner, D.C. Roberts, V. Masson-Delmotte, P. Zhai, M. Tignor, E. Poloczanska, K. Mintenbeck, M. Nicolai, A. Okem, J. Petzold, B. Rama, N. Weyer, IPCC Report on 'The Ocean and Cryosphere in a Changing Climate', 2019.
- [5] State of the climate in 2018, in: J. Blunden, D.S. Arndt (Eds.), *Bull. Am. Meteorol. Soc.* 100 (9) (2019) 1–325, <https://doi.org/10.1175/2019BAMSStateoftheClimate.1>.
- [6] UN United in Science, 2019. https://public.wmo.int/en/resources/united_in_science.
- [7] R.P. Tuckett, *Encycloped. Analyt. Science*, third ed., vol. 4, Elsevier, 2019, pp. 362–372.
- [8] e.g. K.P. Shine, W.T. Sturges, *Science* 315 (2007) 1804–1805.
- [9] R.Y.L. Chim, R.A. Kennedy, R.P. Tuckett, W. Zhou, G.K. Jarvis, D.J. Collins, P.A. Hatherly, *J. Phys. Chem. A* 105 (2001) 8403–8412.
- [10] R.P. Tuckett, *Climate Change/Global Warming: What Can We Do, what Should We Do?* Earth Systems Environmental Sciences, Elsevier, 2018, <https://doi.org/10.1016/B978-0-12-409548-9.11355-7>.
- [11] <https://www.metoffice.gov.uk/about-us/press-office/news/weather-and-climate/2019/state-of-the-uk-climate-2018>.

- [12] US Environmental Protection Agency, Climate Change Indicators and Climate Forcing, 2016, p. 16. <https://www.epa.gov/climate-indicators>.
- [13] <http://www.wmo.int/pages/prog/arep/gaw/ghg/GHGbulletin.html>.
- [14] Intergovernmental Panel on Climate Change (IPCC), 5th Assessment Report (2013), Working Group 1, Chapters 1, 2 and 8, Cambridge University Press, Cambridge, 2013.
- [15] Intergovernmental Panel on Climate Change (IPCC), 4th Assessment Report (2007), Working Group 1, Chapters 1 and 2, Cambridge University Press, Cambridge, 2007.
- [16] L. Cheng, J. Zhu, J. Abraham, *Atmos. Ocean. Sci. Lett.* 8 (2015) 333–338.
- [17] R.A. Hanel, B.J. Conrath, V.G. Kunde, C. Prabhakara, I. Revah, V.V. Salomonson, G. Wolford, *J. Geophys. Res.* 77 (1972) 2629–2641.
- [18] J.G. Anderson, W.H. Brune, M.H. Proffitt, *J. Geophys. Res. D.* 94 (1989) 11465–11479.
- [19] V. Ramaswamy, Intergovernmental Panel on Climate Change (IPCC), 3rd Assessment Report (2001), Chapter 6, Cambridge University Press, Cambridge, 2001.
- [20] M. Etminan, G. Myhre, E.J. Highwood, K.P. Shine, *Geophys. Res. Letts.* 43 (2016) 12614–12623.
- [21] J.H. Butler, S.A. Montzka, The NOAA Annual Greenhouse Gas Index, Spring, 2019. <https://www.esrl.noaa.gov/gmd/aggi/aggi.html>.
- [22] K.P. Shine, J.S. Fuglestedt, K. Hailemariam, N. Stuber, *Clim. Change* 68 (2005) 281–302.
- [23] R.P. Tuckett, *Adv. Fluor. Sci.* 1 (2006) 89–129. Elsevier, ISBN: 0-444-52811-3.
- [24] <http://www.kyotoprotocol.com/resource/kpeng.pdf>.
- [25] R.P. Tuckett, *Educ. Chem.* 45 (2008) 17–21 (Royal Society of Chemistry UK).
- [26] W.T. Sturges, T.J. Wallington, M.D. Hurley, K.P. Shine, K. Sihra, A. Engel, D.E. Oram, S.A. Penkett, R. Mulvaney, C.A.M. Brenninkmeijer, *Science* 289 (2000) 611–613.
- [27] A.R. Ravishankara, S. Solomon, A.A. Turnipseed, R.F. Warren, *Science* 259 (1993) 194–199.
- [28] A. Totterdill, T. Kovacs, W. Feng, S. Dhomse, C.J. Smith, J.C. Gomez-Martin, M.P. Chipperfield, P.M. Forster, J.M.C. Plane, *Atmos. Chem. Phys. Disc.* (2016), <https://doi.org/10.5194/acp-2016-231>.
- [29] A.C. Hong, C.J. Young, M.D. Hurley, T.J. Wallington, S.A. Maburg, *Geophys. Res. Lett.* 40 (2013) 1–6.
- [30] A.R. Ravishankara, E.R. Lovejoy, *J. Chem. Soc. Faraday Trans.* 90 (1994) 2159–2169.
- [31] F.S. Rowland, M.J. Molina, *Rev. Geophys.* 13 (1975) 1–35.
- [32] http://ozone.unep.org/new_site/en/Treaties/treaties_decisions-hb.php?sec_id=5.
- [33] M.P. Chipperfield, S. Bekki, S. Dhomse, N.R.P. Harris, B. Hassler, R. Hossaini, W. Steinbrecht, R. Thieblemont, M. Weber, *Nature* 549 (2017) 211–218.
- [34] Fig. 5 of reference 1. Original figures, 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.
- [35] <http://www.c2es.org/international/negotiations/cop-15/summary>.
- [36] http://www.legislation.gov.uk/ukpga/2008/27/pdfs/ukpga_20080027_en.pdf.
- [37] http://ec.europa.eu/clima/policies/2030/index_en.htm.
- [38] M.R. Allen, Intergovernmental Panel on Climate Change (IPCC), 3rd Assessment Report (2001), Chapter 12, Cambridge University Press, Cambridge, 2001.
- [39] D.J.C. MacKay, *Sustainable Energy – without the Hot Air*, UIT Cambridge UK, 2009. ISBN: 978-0-9544529-3-3.
- [40] V. Quaschnig. https://www.volker-quaschnig.de/datserv/CO2-spez/index_e.php, 2013.
- [41] <http://esa.un.org/wpp>, <http://www.worldometers.info/world-population>.
- [42] G. Monbiot. <http://www.monbiot.com/2009/09/29/the-population-myth>, 2009.
- [43] Population Matters, 2015. <http://www.populationmatters.org>.