

Chapter 2

What Is So Unique About CO₂?

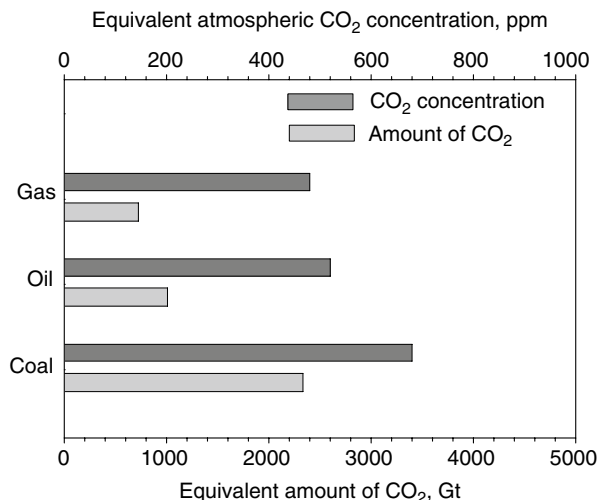
Abstract Considering that the concentration of CO₂ in the atmosphere is extremely low: only 400 ppm or 0.04 vol.%, it is surprising how much impact this gas exerts on life on our planet. What is so unique about CO₂? In this chapter, Greenhouse effect, radiative forcing, global warming potential, global carbon cycle, and other phenomena that control the livability of our planet are linked to unique optical and physicochemical properties of CO₂. An increasing body of scientific evidence suggests that humans are affecting the Earth's radiative and carbon balances mainly through increased emissions of greenhouse gases originating from industrial activities, land-use change, deforestation, and other practices that became prevalent during the rapid industrial development of the last two and half centuries.

2.1 Carbon and Greenhouse Effect

Considering that CO₂ concentration in the atmosphere is extremely low: only 400 ppm, and the overall amount of fossil carbon on our planet is miniscule, 3×10^{-21} wt.%, one can only wonder why there is so much anxiety and agitation in media recently about carbon—“carbon footprint,” “carbon price,” “carbon entanglement,” “carbon tax,” “carbon trading,” “carbon allowances,” “carbon credit,” etc.—and what it has to do with our planet's environment and climate. Since not carbon itself, but the product of its combustion, CO₂, is at the center of the world's attention, then the question becomes: what is so special about CO₂, and how much of it in the air is too much?

Based on the total amount of carbon in fossil fuels, it is easy to estimate how high the atmospheric CO₂ concentration could rise if all the global resources of fossil fuels are burned to CO₂. Figure 2.1 depicts the equivalent amount of CO₂ to be released upon combusting the global resources of major types of fossil fuels: coal, oil, and natural gas (light bars), and the corresponding equivalent atmospheric CO₂ concentration (dark bars).

Fig. 2.1 Equivalent amount of CO₂ corresponding to the global resources of coal, oil, and natural gas (*light bars*), and the equivalent atmospheric CO₂ concentration (*dark bars*). Fossil fuel resources include recoverable reserves and do not include methane hydrates and nonconventional fossil fuels. *Source* [1]



Calculations indicate that if all fossil fuel resources are completely combusted the atmospheric CO₂ concentration would rise to 917 ppm¹ (this value is a net of any carbon absorption by natural sinks). Clearly, this is a hypothetical scenario, and it may never materialize; however, one burning question might arise: can humans live with 917 ppm CO₂ in the atmosphere? Note that this is a miniscule increase—“only” 0.052 vol.%—in the atmospheric CO₂ concentration against the current level, and, besides, CO₂ is a benign gas produced by human body that can tolerate CO₂ concentrations in air many times higher than that. In order to answer this question, let’s first find out what makes CO₂ so unique.

We all know that life on the Earth originated and is sustained due to upcoming solar radiation. Quantitatively, the incident solar radiation flux is equal to about 1,370 W/m², which represents the amount of solar energy hitting 1 m² of the top of the Earth’s atmosphere facing the Sun in 1 s during daytime (If averaged over the entire planet, the amount of received radiant energy would be 341 W/m²) (W is watt, or 1 J/s) [2]. This amount of radiant energy is balanced by a number of energy reflection and emission processes resulting in an equilibrium or zero-energy balance. (Otherwise, the Earth’s surface temperature would have continuously increased.) Roughly a third (102 W/m²) of the incoming solar radiation is reflected back to space by the Earth’s atmosphere, clouds, and aerosols, and the main portion of solar radiant energy (239 W/m²) is absorbed by the Earth’s atmosphere and surface. In order to maintain the energy balance, our planet has to release the same amount of energy back to the space, which it does by emitting radiation. According to the Stefan–Boltzmann law, the amount of radiated energy is proportional to the object’s surface temperature to the fourth power:

¹ppm stands for “part per million”; hereafter ppm relates to volume units (unless otherwise indicated), e.g., 1 ppm=0.0001 vol%.

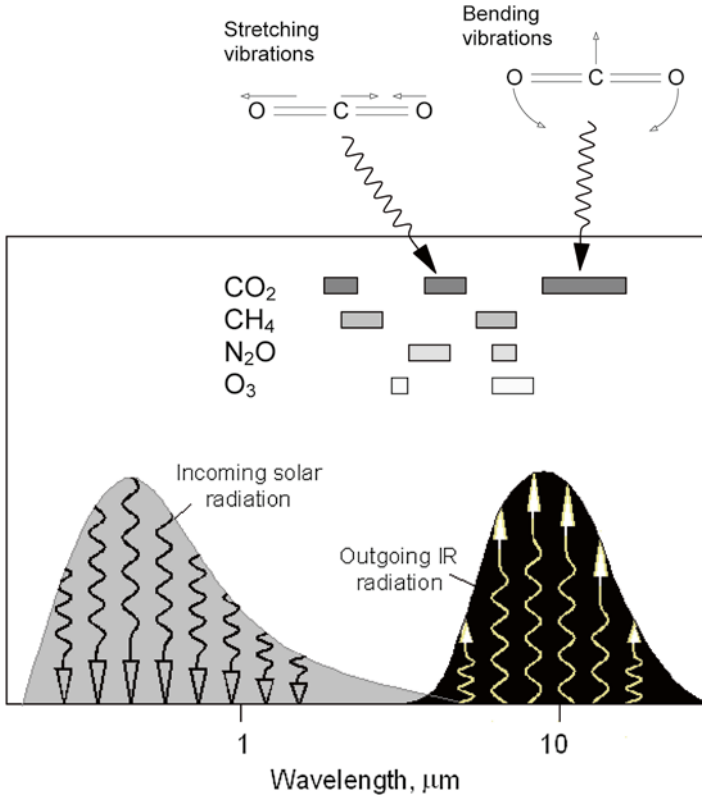


Fig. 2.2 Simplified schematic diagram of greenhouse effect. *Source* [4, 5]

$$E = \varepsilon \sigma T^4 \quad (2.1)$$

where E is the total energy radiated by a body (e.g., in W/m^2), ε is emissivity coefficient, σ is Stefan-Boltzmann coefficient, and T is absolute temperature.

If we estimate the temperature of a body that emits 239 W/m^2 of radiant energy based on this equation, we would arrive to temperature of about -19°C [3], which is far below the average temperature on the Earth's surface: $+14^\circ\text{C}$. That temperature gap of about 33°C is attributed to the presence of heat-trapping agents in the atmosphere called greenhouse gases (GHG): predominantly, CO_2 and water vapor, and, to a smaller extent, methane, ozone (O_3), N_2O and other GHG (note that nitrogen and oxygen—two major constituents of the atmosphere—do not exert such effect for the reasons explained below). GHG absorb and reflect radiant energy within the atmosphere, which in turn emits most of this long wavelength radiation energy back to the Earth's surface and a smaller fraction out to space. Trenberth et al. estimated that an imbalance of 0.9 W/m^2 in the energy fluxes could be attributed to the enhanced greenhouse effect [2]. Figure 2.2 depicts the schematic diagram of the greenhouse effect mechanism involving major heat-trapping gases.

The left curve shows the simplified representation of the spectrum of incoming solar radiation, which includes the wavelengths varying from about 0.2 μm to more than 4 μm , which could be broken down to ultraviolet (UV) light (0.2–0.4 μm), visible light region (0.4–0.8 μm), and infrared (IR) region (longer than 0.8 μm) (μm is micrometer, equal to 10^{-6} m). This curve closely follows the spectrum of a black body heated to about 5,500 K with the peak of the spectral curve in the visible area at about 0.5–0.6 μm . The right curve corresponds to the Earth's radiation spectrum which is associated with black body radiation extending from wavelengths of 1 to 3 μm to about 70–80 μm with the peak at about 10 μm . Due to structural and electronic properties of H₂O_{gas}, CO₂, CH₄, N₂O, and O₃ molecules, they are almost transparent to the upcoming sunlight, but very efficiently (up to 80 %) absorb outgoing IR radiation directed from the Earth surface to the space. The horizontal bars on the diagram correspond to radiation-absorbing capacities of these gases with the length of the bars being approximately proportional to the absorption bandwidth of the corresponding molecules in the IR area of the spectrum (only most important bands are shown).

The common feature of all GHG (e.g., H₂O_{gas}, CO₂, CH₄, N₂O, O₃) is that they contain at least three atoms which allow for a much greater number of fundamental molecular vibrations in response to IR excitation, compared to two-atom molecules (e.g., O₂ and N₂ that do not exert the greenhouse effect). The number of fundamental vibrations for linear three-atom molecules, such as CO₂ is determined by the following formula:

$$V = 3N - 5 \quad (2.2)$$

where V is the number of possible fundamental vibrations and N is the number of atoms in the molecule. (Note that non-linear molecules have $V = 3N - 6$ vibrations.)

Based on the above formula, CO₂ molecule has four vibrations: two stretching (symmetric and asymmetric) and two bending (in-plane and out-of-plane) vibrations (some of them are shown in Fig. 2.2). Thus, CO₂ and other GHG efficiently uptake IR radiation in their respective absorption areas and convert it into thermal vibrational energy (Note that the contribution of H₂O and CO₂ to the greenhouse effect is much greater than that of other GHG due to their relative abundance in the atmosphere.) Collectively, all GHG absorb most of the radiation emitted by the Earth surface leaving a relatively narrow gap permitting some of the thermal radiation to escape into the space and, thus, preventing thermal runaway. In order to further elucidate and quantify the impact of CO₂ and other GHG on the Earth's mean temperature and climate system, it would be useful to introduce the concepts of radiative forcing and global warming potential.

2.1.1 Radiative Forcing Concept

The concept of radiative forcing (RF) has been introduced by IPCC in its early assessment reports for the quantitative comparison of the impact of different natural and man-made drivers on the climate system. RF (expressed in W/m²) is quantified as the rate of radiative energy change per unit area of the globe measured at the top

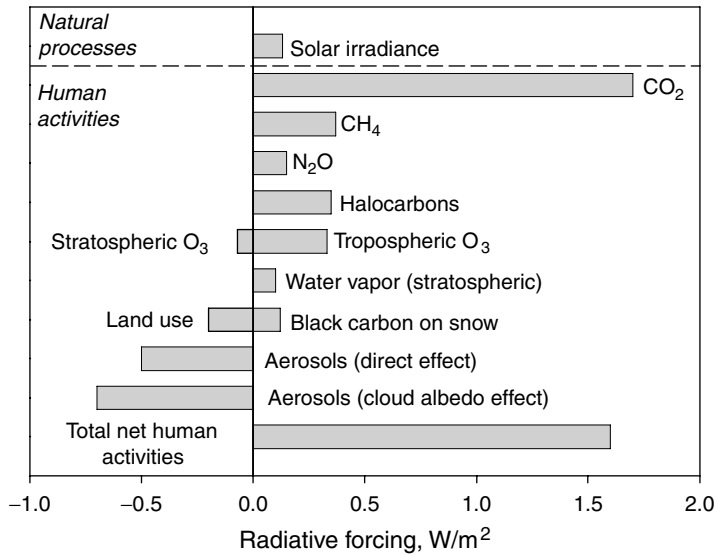


Fig. 2.3 Radiative forcings of the major natural and anthropogenic factors. RF changes since the beginning of the industrial era (ca. 1750) until 2005 are presented. *Source* [6]

of the atmosphere [6]. RF is correlated with the global mean equilibrium temperature change (ΔT_s) at the Earth's surface as follows:

$$\Delta T_s = \lambda \text{RF} \quad (2.3)$$

where λ is the climate sensitivity parameter.

For a greenhouse gas (e.g., CO_2), the change in RF can be calculated as a function of changing CO_2 concentration. For example, in a simplified first-order approximation form, the algebraic expression for ΔRF for CO_2 is [7]

$$\Delta \text{RF} = 5.35 \ln \frac{C_{\text{CO}_2}}{C_{\text{CO}_2}^o} \quad (2.4)$$

where ΔRF is radiative forcing (in W/m^2), C_{CO_2} and $C_{\text{CO}_2}^o$ are the CO_2 variable and reference concentrations, respectively, in ppm.

Since the relationship between CO_2 concentration and radiative forcing (ΔRF) is logarithmic, the increase in atmospheric CO_2 concentrations would have a progressively smaller warming effect. At a typical λ value of 0.8 K per W/m^2 , doubling of CO_2 concentration would result in a mean temperature increase of 3 K.

According to the definition, the RF value is positive when the energy of the Earth–atmosphere system increases (i.e., warming effect), and, correspondingly, the RF is negative if the energy of the Earth–atmosphere system decreases (cooling effect) in response to affecting factors. The RF values for some major natural and human-induced factors are shown in Fig. 2.3.

Natural radiative forcings mainly result from changes in solar irradiance and major volcanic eruptions. Solar source forcing arises from several direct and indirect factors and its value is slightly positive, whereas volcanic eruptions spewing immense amounts of aerosols into the atmosphere create short-lived negative forcing [6]. Human activities have greatly contributed to the changes in radiative forcings since the Industrial Revolution. As can be seen in Fig. 2.3, CO₂ has the greatest increase in the RF values compared to other GHG (all of which have positive RF). The forcing effect of aerosols is rather complex and involves a number of direct (e.g., reflection and absorption of solar and long wavelength radiation in the atmosphere) and indirect (e.g., the changes aerosol particles exert on the optical properties of clouds) effects. The net effect of all aerosol types results in negative RF values. All anthropogenic climate agents, both cooling and warming ones, summarily add up to the forcing value of 1.6 W/m².

Over the last couple centuries (i.e., since the beginning of the industrial era), human activities not only altered the abundance of atmospheric GHG (via burning of fossil fuels) but also changed the land cover over the vast areas on the Earth's surface mainly through agriculture and deforestation. These activities either directly (e.g., via altering the reflectivity of the land surface) or indirectly (e.g., via increasing the CO₂ and CH₄ concentrations in the atmosphere) resulted in appreciable negative changes in the RF values. When assessing the impact of natural factors and human activities on climate system, one should also take into consideration timescales during which a given RF term would persist in the atmosphere after associated emissions or changes are ceased. The available data indicate that the lifetime of various RF factors could last from days for aerosols to 100 years for long-lived GHG and surface albedo (including land use changes) [6].

IPCC 2007 report underscored the interconnection between radiative forcing factors and climate. Figure 2.4 illustrates how RF factor is linked to other aspects of climate change.

Natural processes and influences (e.g., processes on the Sun, volcanoes, changes in the Earth's orbit) as well as human activities (e.g., burning of fossil fuels, industrial GHG emissions, land use) cause direct and indirect changes in the climate change drivers (e.g., release of GHG, aerosols, changes in clouds and solar irradiation, etc.). These changes could lead to specific RF changes (either positive or negative) and noninitial radiative effects (e.g., changes in evaporation). RF and noninitial radiative effects cause climate perturbations and responses. A variety of biogeochemical processes could generate feedback from climate change to its drivers (e.g., increase in methane emissions from wetland during warmer climate). Altering human activities could be one of the potential approaches to mitigating climate change (dashed line).

Recently, the contribution of soot (or black carbon, BC, one of the products of fossil fuel combustion) to overall RF has been revisited [8]. Soot could affect the Earth radiative balance and climate via many routes: absorbing solar radiation, darkening ice and snow, shrinking cloud droplets, etc. The new estimate for the soot RF value -1.1 W/m^2 is roughly twice as large as the RF estimate reported by IPCC in its 2007 report. This puts soot second behind the major RF agent—CO₂—which

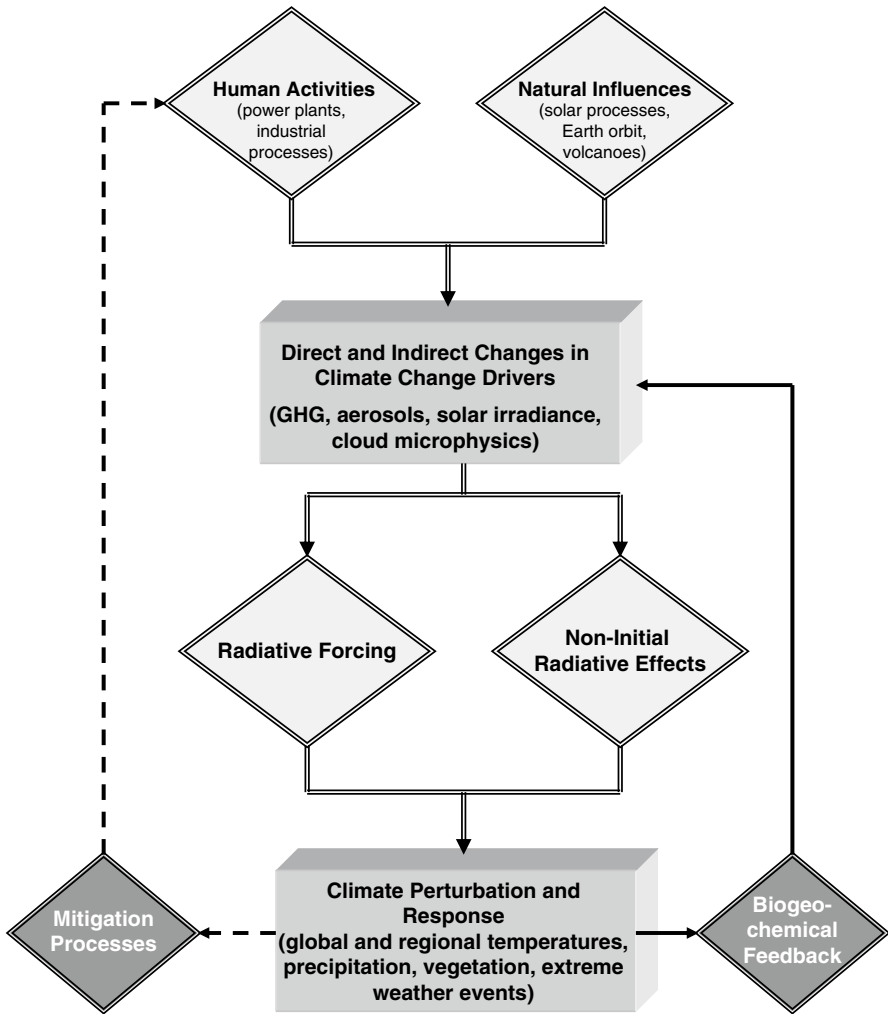


Fig. 2.4 Interconnection between radiative forcing and climate change. *Source* [6]

accounts for 1.66 W/m^2 . On the other hand, many processes that produce BC (e.g., burning of coal or heavy oil) also produce compounds (e.g., sulfur aerosols) that might exert a cooling effect by reflecting sunlight back into space. Forest or brush fires produce soot, but they also produce microscopic particles of unburned organic carbon that can brighten clouds and reflect more radiation, thus, providing some cooling effect. To add to the complexity, besides BC, the atmosphere contains light-absorbing organic “brown” carbon (BrC). According to some estimates, BrC accounts for 15–50 % of light absorption in the atmosphere and in snow and ice [9]. In many climate models, BrC is combined with BC and included in the same

inventories, although they have different optical properties and source and sink patterns. All these factors have to be taken into consideration when estimating the overall RF impact of carbonaceous nano- and microparticles.

The complexity and interplay of the different conflicting factors affecting RF could be underscored by the impact of sulfur-containing particulates. Burning coal is the main way of adding the vast amounts of tiny sulfate particles (sulfate aerosols) in the atmosphere. These particles can either directly (i.e., by reflecting sunlight) or indirectly (i.e., acting as condensation nuclei for cloud formation that reflect solar radiation) cause a cooling effect on climate. Taking this effect into consideration, there has been a counterintuitive conclusion, that if leading world emitters (e.g., the USA, China, India) reduce their particulate emissions in the near future as planned, it would actually contribute to global warming. But the recent findings of the joint project conducted by CICERO and the Norwegian Computing Center indicate that particulate emissions probably have less of an impact on climate through indirect cooling effects than previously thought [10].

Summarizing, the above data clearly indicate that changes in RF resulting from human activities far exceed that from natural sources, which implies that human activities can potentially impact the climate system more profoundly compared to natural sources.

2.1.2 Global Warming Potential of Carbonaceous Gases

Global warming potential (GWP) is a widely used metric tool that provides a means of comparing the capacity of different greenhouse agents to contribute to global warming. GWP of CO₂ is accepted as a unity (i.e., GWP_{CO₂} = 1). GWP of a greenhouse agent is determined by two main factors: (a) its capacity to absorb IR radiation (which is linked to its spectral properties), and (b) its lifetime in the atmosphere. The greater IR absorption capacity and longer atmospheric lifetime of the agent would result in its greater GWP values. In order to calculate GWP of the agent i , the time-integrated global mean RF value of the agent (i) 1 kg of which was pulse emitted to the atmosphere is to be divided by the corresponding RF value of the reference gas CO₂ as follows [11]:

$$GWP_i = \frac{\int_0^{TH} RF_i(t) dt}{\int_0^{TH} RF_{CO_2}(t) dt} = \frac{\int_0^{TH} a_i [C_i(t)] dt}{\int_0^{TH} a_{CO_2} [C_{CO_2}(t)] dt} \quad (2.5)$$

where TH is a time horizon, RF _{i} is the global mean RF of the agent i , a_i is the RF per unit mass increase in atmospheric abundance of the agent i , and $[C_i(t)]$ is the time-dependent abundance of the agent i . The denominator includes the corresponding values for the reference gas CO₂.

Table 2.1 Global warming potentials of selected greenhouse gases for the time horizons of 20 and 100 years

Greenhouse gas	Time horizon (years)	
	20	100
Methane (CH ₄)	72	25
Nitrous oxide (N ₂ O)	289	298
Chlorofluorocarbon (CCl ₂ F ₂)	11,000	10,900

Source [12]

GWP values for major GHG for the time horizons of 20 and 100 years (average uncertainty of the GWP values are $\pm 35\%$) are shown in Table 2.1.

GWP values for the different GHG vary in the wide range: from a few units to tens of thousands. GWP of methane is 72 and 25 times greater than that of CO₂ over the time horizon of 20 and 100 years, respectively. GWP of N₂O and chlorofluorocarbons are about 300 times and 4 orders of magnitude greater than that of CO₂, respectively (Note that they do not change markedly over the shown time horizon.) The above data indicate that compared to other GHG, CO₂ is a rather mild greenhouse agent, but, nevertheless, it can exert a profound impact on the climate system for the reasons explained below.

2.2 Trends in Atmospheric Greenhouse Gases

2.2.1 Increase in Atmospheric CO₂: Natural vs. Human-Induced Factors

The atmospheric CO₂ concentration has been measured with a great accuracy since the 1950s by C. Keeling at Mauna Loa, Hawaii (USA) using a high-precision IR gas analyzer. Since then, continuous CO₂ measurements are being conducted at other sites in both hemispheres: Baring Head (New Zealand), Cape Grim (Australia) and South Pole (the selection of these particular locations is dictated by the lack of significant CO₂ sources or sinks nearby). The results of direct and indirect measurements of atmospheric CO₂ level imply that it has increased from preindustrial concentration of 275–285 ppm to the benchmark 400 ppm measured in May 2013 by Mauna Loa Observatory (i.e., the growth by 45 % over two and half centuries) [6, 13]. The measurements also indicated that the rate of CO₂ growth is accelerating: the average annual rate of increase was 0.7 ppm per year during the 1950s, 1.4 ppm per year during 1955–1995, and 1.9 ppm per year during 1995–2005 [13, 14]. In its 2007 report, IPCC projected the rate of CO₂ growth at 1.9 ppm per year [6], but these projections have proved rather conservative, because during the decade of 2002–2011, the CO₂ growth rate increased to 2.07 ppm per year [14].

In order to ascertain whether this increase in atmospheric CO₂ concentrations is due to natural causes or the result of human activity, let's consider several factors:

- There is a clear correlation between the amount of anthropogenic CO₂ released to the atmosphere and the increase in atmospheric CO₂ concentration during last decades.
- Atmospheric oxygen is declining proportionately to CO₂ increase and fossil fuel combustion.
- For the last half century, the CO₂ airborne fraction (AF) parameter remained consistent and averaged at 0.55 (the AF parameter is the ratio of the increase in atmospheric CO₂ concentration to fossil fuel-derived CO₂ emissions). AF has been introduced to assess short- and long-term changes in the atmospheric carbon content; in particular, AF of 0.55 indicates that the oceans and terrestrial ecosystems have cumulatively removed about 45 % of anthropogenic CO₂ from the atmosphere over the last half century [6].
- The isotopic signature of fossil fuels (e.g., the lack of ¹⁴C and the depleted level of ¹³C carbon isotopes) is detected in atmospheric CO₂.
- There exists an interhemispheric gradient in the atmospheric CO₂ concentrations in the Northern and Southern Hemispheres. In particular, the predominance of fossil-derived CO₂ emissions in more industrially developed Northern Hemisphere (compared to the Southern Hemisphere) causes the occurrence of the atmospheric CO₂ gradient in the amount of about 0.5 ppm per GtC per year [6].
- There have been dramatic changes in RF_{CO2} values over the last decades. For example, during 1995–2005, the RF_{CO2} increased by about 0.28 W/m² (or about 20 % increase), which represents the largest increase in RF_{CO2} for any decade since the beginning of the industrial era. RF_{CO2} in 2005 was estimated at RF_{CO2} = 1.66 ± 0.17 W/m² (corresponding to the atmospheric CO₂ concentration of 379 ± 0.65 ppm), which is the largest RF among all major forcing factors shown in Fig. 2.3.
- The data show that the changes in the land use greatly contributed to the RF_{CO2} value in the amount of about 0.4 W/m² (since the beginning of the industrial era). This implies that the remaining three quarters of RF_{CO2} can be attributed to burning fossil fuels, cement manufacturing, and other industrial CO₂ emitters [6].

The above facts suggest it is *extremely likely* that there is a link between the increase in the atmospheric CO₂ concentration and the greater than before levels of CO₂ emissions from human activities. The IPCC 2013 Assessment Report underscored that “*The atmospheric concentrations of greenhouse gases carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) have all increased since 1750 due to human activity*” [15]. Atmospheric concentrations of these gases substantially exceed the highest concentrations recorded in ice cores during the past 800,000 years, and the mean rates of their increase over the past century are (with very high confidence) unprecedented in the last 22,000 years [15].

In the next sections, the potential impact of two other major GHG, water vapor and methane, on our planet's ecosphere and climate will be discussed. Other GHG (N₂O, ozone, halocarbons) are out of scope of this book; the information on these GHG could be found in [6] and other publications.

2.2.2 Role of Water Vapor

Water vapor is the most abundant and dominant GHG in the atmosphere and one of the key variables of the climate system. Water vapor accounts for the lion's share of IR absorption in the atmosphere (according to some estimates, about 60 % of the natural greenhouse effect, for clear skies) [16]. The atmospheric concentration of water vapor depends largely on temperature and varies in a very wide range, from less than 0.01 % in extremely cold regions up to 3 % by mass in saturated air at about 32 °C [17]; compared to other GHG, it is neither long-lived nor well mixed in the atmosphere. As an additional distinction from other GHG, atmospheric water can exist in several physical states: gaseous, liquid, and solid (these forms of water can coexist in the atmosphere for a short period of time).

Despite the abundance of water vapor in the atmosphere, it is believed that human activities *do not directly* affect the average global concentration of water vapor in the atmosphere (stratospheric water vapor has relatively low RF value). However, the radiative forcing produced by the increased concentrations of other greenhouse gases may *indirectly* affect the hydrologic cycle. As a result, human activities could profoundly *indirectly* affect the atmospheric water vapor concentration and, ultimately, the climate system, via a number of mechanisms. For example, the accumulation of CO₂ (or CH₄) could lead to warming of the atmosphere and increasing its water vapor content by enhancing the evaporation process. Studies show that for every 1 °C increase in the global temperature, the specific humidity rises in average by 5.7 % and 4.3 % over the ocean and land surfaces, respectively (global average is about 4.9 % increase per 1 °C) [6]. Warmer atmosphere via an increased water holding capacity (i.e., increased concentrations of water vapor) could potentially affect the formation of clouds, which can either absorb or reflect solar radiation.

Aircraft contrails, which consist of water vapor and other aircraft exhausts, have a radiative forcing effect similar to that of clouds [18]. Another mechanism dealing with the indirect effect of water vapor formation in the stratosphere involves photochemical oxidation of organic and inorganic compounds originating from human activities, such as anthropogenic methane, ammonia, uncombusted hydrocarbons, H₂S, and volatile organic compounds. Due to the sensitivity of water vapor content to temperature, a variety of models predict that this factor could provide the largest positive feedback with regard to the climate system [19] (see discussion of the water vapor feedback mechanism in Sect. 2.5.3).

A direct link between the changes in the concentration of stratospheric water vapor and mean surface temperature has been reported by a group of scientists from the US National Oceanic and Atmospheric Administration (NOAA) and other institutions [20]. It was shown that stratospheric water vapor concentrations gradually increased between 1980 and 2000 causing a near decade-long (1990–2000) warming by about 30 % (compared to the scenario neglecting this change). However, since 2000, the stratospheric water vapor concentration dropped by about 10 %,

which is consistent with the observation of global surface temperature remaining almost flat since the late 1990s, despite ongoing increases in GHG emissions. These trends indicate that stratospheric water vapor is a very important factor in global surface temperature variations, and the terms related to water vapor impact should be fully represented in advanced climate models.

2.3 Methane: Just Another Greenhouse Gas or a Sleeping Giant?

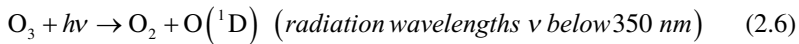
About 55 million years ago (during the Paleocene–Eocene Thermal Maximum, PETM), our planet experienced “a hot flash,” i.e., sudden surge in surface temperature, which lasted for over hundred millennia [21]. Many researchers linked that extreme warming to a dramatic perturbation of the Earth’s carbon cycle caused by massive methane emissions. What event or phenomenon triggered these massive methane emissions is still open to debates. But even more important question remains: if this giant outbreak of methane so dramatically impacted the global radiative energy balance and climate, could this happen again? Indeed, some scientists raised alarm that one of the dire consequences of the climate change could be the widespread liberation of (currently dormant) immense quantities of methane gas trapped in the marine and permafrost sediments [22–25].

2.3.1 Methane as a Potent Greenhouse Gas

As GHG, methane (CH₄) is significantly more potent than CO₂ (based on its GWP values), and it has second (next to CO₂) largest radiative forcing ($RF_{CH_4} = 0.48 \pm 0.05 \text{ W/m}^2$) among all GHG (see Fig. 2.3); as such, it could potentially exert a substantial impact on the global radiative energy balance and, consequently, climate. While the IPCC 2007 report [6] recommended GWP_{methane} values of 25 and 72 over integrated 100 and 20 years time horizons, respectively, more recent data reported by Shindell et al. in *Science* magazine indicate that better accounting for the interaction of methane with other radiatively active matter in the atmosphere would put mean GWP_{methane} values at 105 and 33 for the same 20 and 100 years time horizon, respectively [26]. Using this value of methane GWP, Howarth et al. estimated that methane would be responsible for 44 % of the warming impact of the entire US GHG inventory (including CO₂ and other man-made emissions) over 20 years time frame [27]. An important implication of these data was that, in the short term, the climate system is more responsive to changes in methane emissions than CO₂ emissions [28]. This underscores the urgency of taking immediate and strong measures to reduce methane emissions worldwide.

Although methane is a very potent GHG, in contrast to CO₂, it does not remain in the atmosphere for too long: its residence time in the atmosphere is estimated at

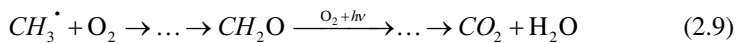
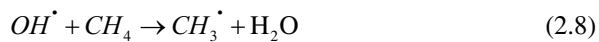
8.4 years [6] (compared to hundreds years for CO₂). Methane is primarily removed (via oxidation to CO₂) from the atmosphere via a chain of chemical and photochemical reactions involving very reactive hydroxyl radicals (OH[•]), the primary source of which is UV-assisted ozone photodissociation in the presence of water vapor [29]:



where O(¹D) is an electronically excited state of oxygen atom, and $h\nu$ is a light photon



OH[•]-radicals attack methane molecules converting them first into oxygenated compounds (e.g., formaldehyde, CH₂O) and then to CO₂ and water as follows:



Thus, methane released to the atmosphere is gradually converted into CO₂ and ultimately increases CO₂ levels in the atmosphere. Other important methane sinks include biological oxidation in soil, the loss to the stratosphere, and reactions with halogen (e.g., Cl[•]) radicals. The amount of methane removed by the sinks is estimated at 581 Mt (CH₄) per year [6].

2.3.2 Historical Trends in Atmospheric Methane Concentration

Over the last millennia, the atmospheric methane concentration varied in the range of 400–700 parts per billion (ppb) [30]. Similar to CO₂, the atmospheric concentration of methane has dramatically increased since the beginning of the Industrial Revolution. The atmospheric CH₄ concentration measurements conducted in the Northern (Mace Head, Ireland) and Southern (Cape Grim, Tasmania) hemispheres gave the values of 1,865 and 1,741 ppb, respectively [31]. In 2011, the atmospheric concentration of methane was 1,803 ppb [15]. Although this value is about 200 times less than that of CO₂, one should take into consideration that its concentration has risen by about 150 % since preindustrial times, compared to about 45 % for CO₂ [15, 32].

Atmospheric methane concentration is controlled by the balance between its sources (both natural and anthropogenic) and sinks. The major natural sources of methane are wetlands, permafrost, vegetation, termites, oceans, methane hydrates, and geothermal sources (mud volcanoes, marine and land seepage, etc.). The amount of methane (in carbon equivalent) in wetlands and permafrost (subsea and soils)

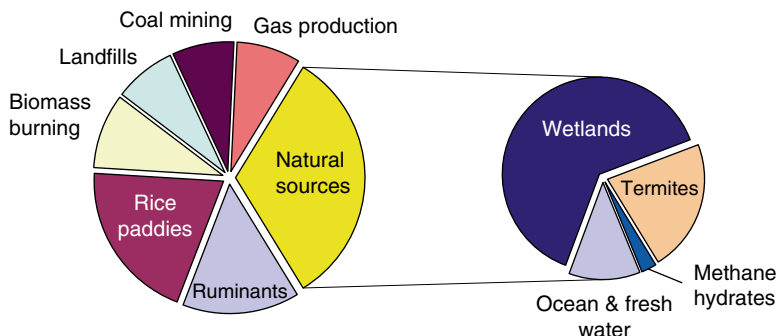


Fig. 2.5 Relative distribution of natural and man-made methane emissions from different sources. Source [35]

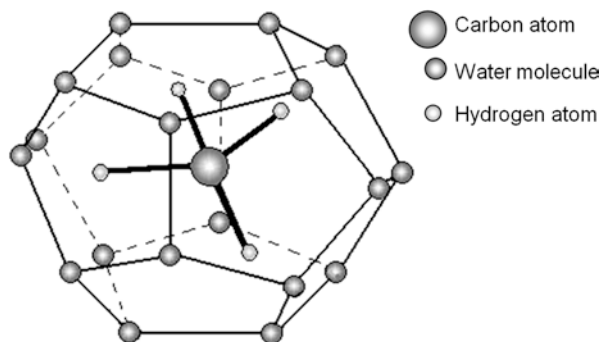
is immense: it is about twice the amount of CO₂ in the atmosphere [33]. The anthropogenic sources of methane include natural gas processing facilities, fossil fuel production and use, coal mining, landfills, ruminant animals (cattle, sheep, etc.), rice agriculture, biomass processing, and combustion. Methane emissions from living vegetation accounts for 10–30 % of the total methane emissions [34]. Figure 2.5 shows relative distribution of methane emissions from different sources. The overall amount of atmospheric methane is estimated at 4,932 Mt (CH₄) [6].

The available data indicate that although the atmospheric methane concentration increased by about 30 % over the last quarter of a century, its growth rate substantially slowed down in the late 1990s. There are several explanations to this phenomenon. Based on the comparison of isotopic signatures of methane from fossil fuels and microbial sources, researchers at the University of California have come to a conclusion that this decline is partly due to an increase in fertilizer use combined with decreased water use in Asian rice agriculture [36]. An alternative explanation of the slowdown in methane emission rate links it to the decrease in the rate of fossil fuels combustion beginning in the 1980s. This conclusion was based on measurements of the concentration of trace gas, ethane, in air bubbles in Greenland and Antarctica (Note that ethane and methane are both produced during fossil fuels combustion.) and a relevant atmospheric model [36]. These conflicting conclusions illustrate the complexity of the physico-biochemical processes behind this phenomenon.

2.3.3 Natural Sources of Methane

A potential impact of methane on the Earth's climate system is linked to the high sensitivity of methane biochemistry to temperature and water level changes. Several authors reported a significant increase in CH₄ emissions from northern peatlands due to permafrost melting [37]. The results of modeling studies indicate that methane emissions from Scotland wetlands could increase by 17, 30, and 60 % if climate warms up by 1.5,

Fig. 2.6 One of possible structures of methane hydrates: 12-hedron (Dodecahedron)



2.5, and 4.5 °C, respectively [38]. Based on simulation studies, Shindel et.al. [39] projected that doubling in the atmospheric CO₂ concentration would result in warming by 3.4 °C, and, consequently, in 78 % increase in CH₄ emissions from wetlands.

2.3.3.1 Methane Hydrates

No other source of methane emissions instigates so much concern and fear with regard to its potentially destructive impact on climate and life on our planet as methane hydrate (it is often referred to in the literature as “*ticking time bomb*,” “*the harbinger of impending catastrophe*,” “*a sleeping giant*” [24]. (Methane hydrate as a potential source of unconventional gas is discussed in Chap. 1.) Methane hydrate is an ice-like solid substance formed from methane and water molecules under high pressure (greater than 3–5 MPa, which corresponds to water/sediment depths of 300–500 m) and relatively low temperature (up to about 25 °C) [40], and can be represented by a general formula CH₄·*n*H₂O (the nominal methane clathrate composition is CH₄·5.75H₂O). Figure 2.6 depicts the diagram of one of the possible methane hydrate structures.

Methane hydrate can be easily transformed back to gas if one or both parameters (i.e., pressure or temperature) are altered such that hydrate molecules move out of the thermodynamic stability zone. When destabilized, one cubic meter of methane hydrate releases 164 m³ of methane (at near ambient conditions) [41]. One of the main causes of methane hydrate destabilization that worries the majority of climate scientists relates to the increase in global mean temperature. In principle, the susceptibility of gas hydrates to warming climate depends on a number of factors, such as the duration of the warming event, the depth at which methane hydrates lie beneath the ocean floor or tundra surface, and the amount of heat required to warm up sediments to the point of hydrates dissociation.

Methane hydrates typically occur in shallow sediments in cold regions (e.g., Arctic area) or in deep-water (depths greater than 500–600 m) marine sediments where sufficiently low temperature and high-pressure conditions favor forming and sustaining of the hydrates. Methane that forms hydrate can be of *biogenic* nature (created by biological activity in sediments, e.g., the microbial decomposition or

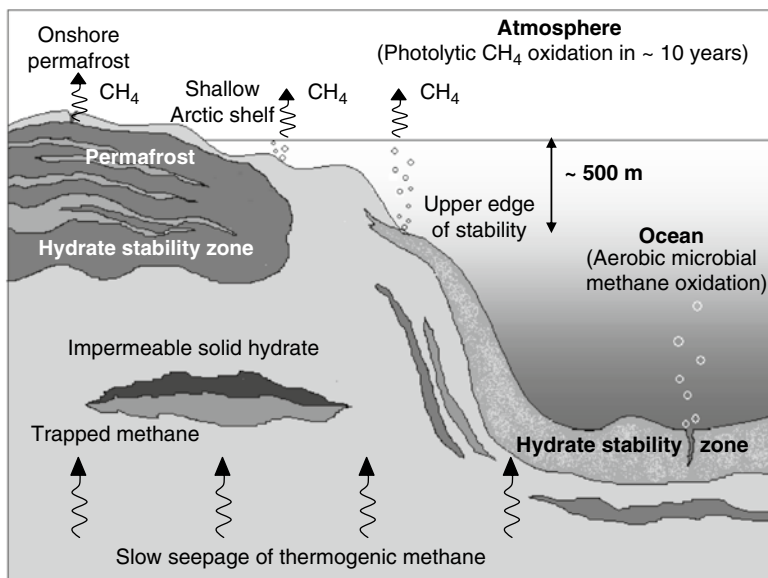


Fig. 2.7 Diagram of different methane hydrate deposits. *Source* [40]

deep burial and/or heating of organic matter) or *thermogenic* nature (created by geological processes deep within the Earth crust). Most of the Earth's methane hydrates (estimated at about 95 %) occur in the ocean depths greater than 1,000 m (where an estimated amount of $\sim 4 \times 10^6$ million ton of CH₄ are stored [42]), and their stability is another unknown in climate change models. Figure 2.7 provides a schematic diagram of different methane hydrate deposits.

It was estimated that, currently, about 2 % of atmospheric methane might have originated from dissociation of global deposits of methane hydrates (this is a rough estimate, because there are no tools available to scientists that can distinguish between methane originated from methane hydrates or other sources) [35].

The fate of methane hydrates during warming climate is a highly debated subject. In recent years, a number of research and popular articles have put methane hydrates in focus of the climate change dispute and explored consequences of a catastrophic methane outburst for our civilization [22–24, 43, 44]. It has been emphasized that even if only a fraction of liberated methane was to reach the atmosphere, its strong heat-trapping properties combined with the persistence of its oxidation product (CO₂) could potentially represent a tipping point for the Earth's carbon cycle and contemporary period of climate change [25, 43]. Modeling studies showed that the anthropogenic CO₂ could cause the release of about 2,000 Gt of methane from hydrates, and the increase in deep-water temperature of 3 °C would result in the release of about 85 % of methane from methane hydrates [42].

What fuels the fears most is that, according to available data, such a historical large-scale climate-driven destabilization of methane hydrates on a global scale has already occurred in the past: extreme warming during PETM is attributed to a massive release of methane from global methane hydrates [40]. Some climate scientists advanced the “*clathrate gun*” hypothesis, which postulates that repeated warming of intermediate ocean waters triggered periodic catastrophic dissociation of methane hydrates during the Late Quaternary taking place 400,000–10,000 years ago [35, 45]. Of particular worry is the fact that climate changes in the past were incredibly rapid. The research on Red Sea sediments shows that during the last warm period between ice ages (about 125,000 years ago), sea levels rose and fell by as much as 2 m within a century [46]. Also surprising is how little forcing was required to trigger past climate swings, e.g., research shows that PETM was apparently sparked by a preceding increase of about 2 °C in the Earth’s temperature, which was already warmer than today. That warming may have been amplified by positive feedback mechanisms [47].

Less alarming voices could also be heard in the dispute over potential climate perturbations due to methane hydrates destabilization. Carolyn Ruppel, the head of the US Geological Survey’s Gas Hydrates Project, suggests that if our planet’s warming continues at rates documented by IPCC for the twentieth century (0.2 °C per decade), this should not result in catastrophic breakdown of methane hydrates and major leakage of methane to the ocean–atmosphere system [40]. She holds that most of the methane hydrates would have to experience sustained warming over thousands of years before their massive destabilization could be triggered, although, in some places, methane hydrates could dissociate now in response to short- and long-term climatic processes.

Different types of methane hydrates could experience different rates of dissociation. For example, methane hydrates beneath thick onshore permafrost (lying deeper than about 190 m below the Earth’s surface) will remain largely stable even if climate warming lasts hundreds of years. On the other hand, subsea permafrost beneath shallow Arctic shelf is thawing, and associated methane hydrates are likely dissociating now. Luckily, only 1 % of the world’s methane hydrates probably occur in this setting (but this estimate could be revised as more data become available). Methane hydrates occurring in upper continental slopes, beneath 300–500 m of water, lie at the borderline of hydrates thermodynamic stability. Methane hydrates exposed to warming ocean waters could completely dissociate in less than hundred years; however, due to dissolution and aerobic oxidation in the water column, only a fraction of released methane will likely reach the atmosphere. About 3.5 % of the global methane hydrates occur in this climate-sensitive setting [35, 40].

Geophysical calculations conducted by the Ruppel’s group indicate that over 10, 100, and 1,000 years, the methane hydrates lying at the depths of 18 m, 56 m, and 178 m, respectively, will be affected by warming climate [40]. Even over 1,000 years time horizon, only methane hydrates located close to the seafloor and approaching the thermodynamic stability boundary (about 5 % of the total methane hydrate inventory) might experience dissociation in response to reasonable rates of warming. There are several factors that can alleviate the impact of liberated methane on

the ocean-atmosphere system and, ultimately, on climate. First, in marine sediments, the released methane may remain trapped as gas, and up to 90 % of methane that reaches the near-seafloor sediments (especially, in sulfate reduction zone) may be consumed by anaerobic microbial oxidation [48, 49]. Second, methane bubbles released at the seafloor rarely survive the trip to the surface. At the depths greater than about 100 m, dissolved oxygen and nitrogen almost completely replace methane within the rising bubbles; methane dissolved in the water column becomes an easy target of aerobic microbes that serve as an important sink for methane over a wide depth range [50].

Although microbial oxidation of methane in water column mitigates its direct impact as GHG, it also depletes dissolved oxygen and generates oxidation product CO₂, hence, leading to the acidification of ocean waters and eventual release of CO₂ to the atmosphere after residence times of less than 50 years to several hundred years (from water depths of up to 500 m to more profound depths, respectively) [40, 51]. According to Ruppel's calculations, even in the unlikely event that 0.1 % (or 1.8 GtC) of global methane inventory of $\sim 1.8 \times 10^3$ GtC in hydrates (according to [52]) was instantaneously released to the atmosphere, CH₄ atmospheric concentrations would increase to $\sim 2,900$ ppb from the 2005 value of $\sim 1,774$ ppb (according to [6]), i.e., by 63 % [40] (or by about 1 ppm). Considering that this would be an isolated incident, the warming is supposed to be relatively short-lived given the relatively short atmospheric residence time for methane (about a decade). According to the study, CO₂ produced by the oxidation of CH₄ released from dissociating methane hydrates will likely have a greater impact on the Earth ecosystems (e.g., on ocean chemistry and atmospheric CO₂ concentrations) and climate than will methane that remains after passing through various sinks.

Summarizing, although there appears to be a consensus against the looming methane-induced catastrophe (at least in the short-to-mid term), the available scientific information highlights gaps in our understanding of the methane release impact on climate, and points to the need for monitoring of changes to the methane cycle and the development of better models to predict future changes.

2.3.3.2 Permafrost

Methane hydrate is not the only natural source of methane emissions to the atmosphere. As can be seen from Fig. 2.6, tropical wetlands, agriculture, landfills, and fossil fuel production are much bigger players (cumulative annual global methane emissions are estimated at 440–500 million tons CH₄ of which anthropogenic emissions make up about 60 %). [21, 33]. It has been reported that methane is leaking out of thawing permafrost and regions of glacial retreat across Alaska (estimated at about 2 million tons of methane per year) [53]. The researchers emphasized that the most active sites emitting “old” biogenic methane occur in the areas that have only recently lost their capping ice due to warming. If warming continues, this could pop-up the “cork” and lead to a relatively rapid release (pulse) of methane into the atmosphere.

A recent study conducted by Russian researchers reported that a large amount of methane is seeping into the atmosphere from East Siberian Arctic Shelf (ESAS) sediments [54]. The authors of the study attributed the sustained release of methane from thawing Arctic permafrost to perforations in the seal due to ongoing warming and a possible positive feedback effect. The annual methane outgassing from the shallow ESAS areas was estimated at about 8 million ton CH_4 per year, which is of the same magnitude as the total methane emissions from all the oceans. The authors of the study contend that although the amount of methane emissions seems to be insignificant compared to cumulative global emissions of methane (only about 2 % of the total 440–500 million ton), in a worst-case scenario, it could signal the triggering of worrisome positive feedback and the beginning of massive methane release with unpredictable consequences for climate.

The importance of permafrost factor is that it could completely throw off global climate change forecasts, because existing models and scientific assessments (including those of IPCC) don't factor in the emissions from thawing permafrost. The United Nations Environment Programme (UNEP) 2012 report points out that human-induced climate change is expected to cause significant amounts of permafrost to thaw [55]. As a result, organic material in the soil frozen for millennia (which is found beneath 24 % of exposed land in Northern Hemisphere, i.e., under tundra, boreal forests, and alpine regions) will decompose and irreversibly release both CO_2 and CH_4 [56].

Most of the current permafrost was formed during or since the last Ice Age and extends to depths of more than 700 meters in parts of northern Siberia and Canada and contains 1,700 Gt of carbon (twice the amount currently in the atmosphere). Once the thawing process begins, it will trigger a feedback loop known as the *permafrost carbon feedback* (see Sect. 2.5.3.4 for details), which has the effect of accelerating the further warming of permafrost—a process that would be irreversible on a human life timescale. Warming permafrost could emit 43–135 Gt of CO_2 equivalent by 2100 and 246–415 Gt by 2200 [55]. The emissions could start within the next few decades and continue for several centuries, ultimately accounting for up to 39 % of total emissions. According to the UNEP report [55], Arctic and alpine air temperatures are expected to increase at roughly twice the global rate: a global temperature increase of 3 °C would mean a 6 °C increase in the Arctic, resulting in an irreversible loss of anywhere between 30 and 85 % of near-surface permafrost.

Warming permafrost could bring negative consequences in terms of both ecosystems and infrastructure damage. Since thawing permafrost is structurally weak, it may result in foundational settling that can damage or even destroy buildings, roads, pipelines, railways and power lines (For example, in the 1994, the pipeline to the Vozei oilfield in northern Russia, was broken down, resulting in a spill of 160,000 t of oil, the world's largest terrestrial oil spill.) [55]. Economic impact of permafrost thawing could be huge: it could add up to US\$6.1 billion to future costs for public infrastructure in the US state of Alaska between now and 2030. UNEP report recommends that permafrost emissions must be factored into the treaty addressing global climate change expected to replace the Kyoto Protocol. In particular, the

IPCC may consider preparing a special assessment report on how CO₂ and methane emissions from warming permafrost would influence global climate change policies. The report also recommends the countries with the most permafrost: Russia, Canada, China, and the USA, to initiate adaptation policies, and evaluate the potential risks, damage and costs of permafrost degradation to critical infrastructures.

2.3.3.3 Wetlands

Wetlands are another potential source of methane emissions. Estimated 39 % of global methane emissions originate from natural and agricultural wetlands [57]. Wetlands are significant carbon sinks, storing about 20 % of the world's soil carbon in only 5 % of land [58]. However, if more lands become submerged due to rising temperatures or sea-level rise, methane and nitrous oxide (N₂O) could be released, which will change wetlands from being a net sink to a net source of GHG emissions.

A wide variety of wetlands with a broad range of GHG fluxes could be found around the world from high latitudes to tropical zones. In wetlands located in temperate and tropical zones, water depth and temperature changes determine whether these wetlands are net sources or sinks of methane emissions. It is very difficult to quantify the amount of carbon sequestration and methane emissions in wetlands using existing computer models, since many factors need to be considered including variability in landscape, salinity, and plant species.

2.3.4 Anthropogenic Sources of Methane

Methane emissions linked to human activities make up almost two-thirds of the overall methane emissions to the atmosphere. In the USA, in 2011, total methane emissions amounted to 551 Tg CO₂-equiv., which is about 8.2 % of all GHG (i.e., CO₂, CH₄, N₂O, and halocarbons) emissions from all sources amounting to 6,708 Tg CO₂-equiv. [59] (Tg is teragram, or 10¹² g). Figure 2.8 depicts the contributions of different sources (energy sector, agriculture, waste, etc.) to overall methane emissions in the USA in 2011.

NG systems and agriculture are two major sources of man-made methane emissions. Agricultural processes such as wetland rice cultivation, enteric fermentation in animals, and the anaerobic decomposition of animal wastes and municipal solid waste (MSW) emit large amounts of CH₄. Methane is also emitted during the production, transportation, and distribution of NG and petroleum, and it is released as a by-product of coal mining and incomplete fossil fuel combustion (methane emissions from NG systems are discussed in more details in Sect. 8.2.4).

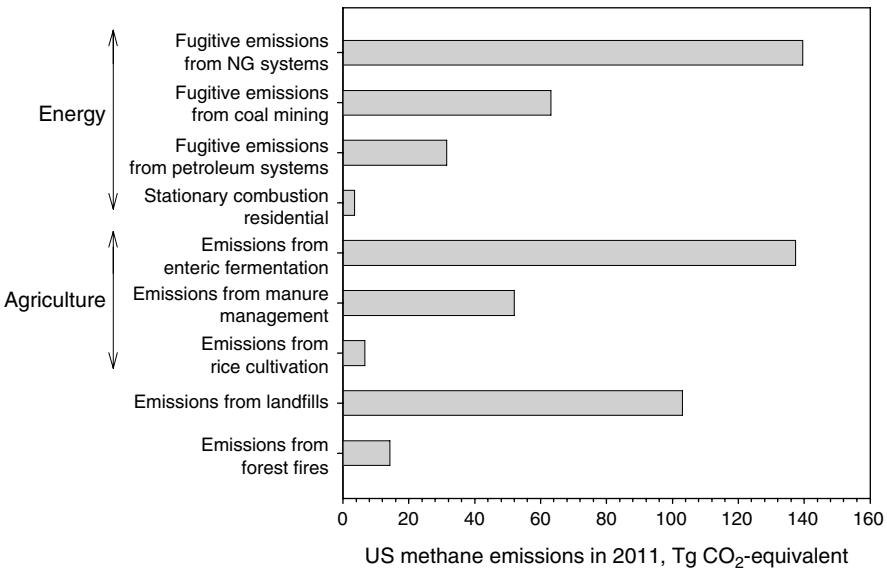


Fig. 2.8 Inventory of US methane emissions from human activities. *Source* [59]

2.4 Global Carbon Cycle

Carbon cycle is a series of cyclic processes by which carbon is exchanged between four major carbon reservoirs: atmosphere, geosphere, hydrosphere, and biosphere. Over geological time, photosynthetic CO₂ fixation exceeded respiratory oxidation of organic carbon to CO₂, which resulted in the reduction of CO₂ to organic carbon followed by its burial in marine sediments [60, 61]. The amount of carbon exchanged between the major carbon reservoirs depends on a variety of factors that are yet to be fully understood. There are several versions of the carbon cycles reported in the literature; in all of them, CO₂ plays a critical role as an exchange “currency” between the reservoirs (in some versions of the carbon cycles, methane is also involved but it plays a minor role). Figure 2.9 depicts a simplified schematic diagram of one version of the natural carbon cycle. It shows unperturbed carbon exchanges between the ocean, the atmosphere, and land in the form of arrows with the values of the carbon fluxes between the reservoirs shown by numbers between the arrows (in GtC/year).

In this diagram, the positive value of the carbon flux indicates carbon input to the atmosphere (e.g., fossil-derived emissions plus emissions from cement manufacturing plants), and negative flux values correspond to carbon losses from the atmosphere to sinks.

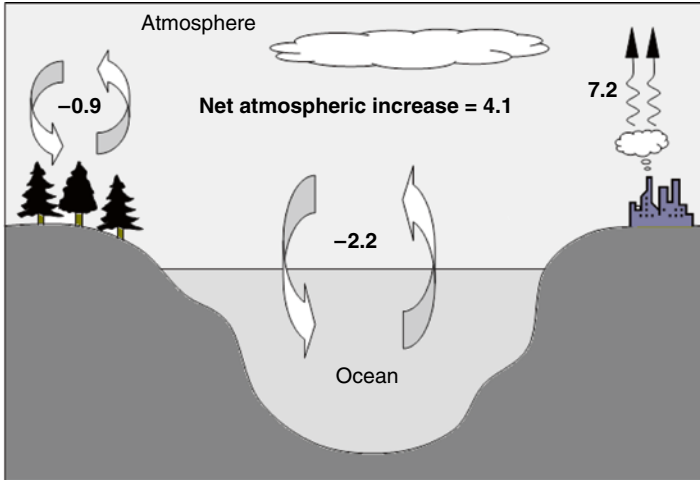


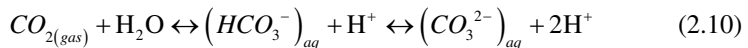
Fig. 2.9 Simplified schematic diagram of the natural carbon cycle. Source [6]

2.4.1 Ocean and Terrestrial Carbon Cycles

2.4.1.1 Ocean Carbon Cycle

CO₂ exchange between the atmosphere and the ocean is a relatively slow process: the timescale for reaching equilibrium between the atmosphere and the ocean surface depends on many factors such as wind speed, temperature, precipitation, and heat flux, and the majority of estimates agree on a timeframe of about 1 year. It was determined that the rate-limiting step of the overall atmosphere–ocean exchange process is the rate of the mixing of surface waters with the intermediate and deep ocean, which is much slower process than air-sea gas exchange. In principle, the ocean can theoretically absorb up to 70–80 % of the anthropogenic CO₂ emissions, but it would take several centuries to complete that due to the slow surface-deep ocean exchange rate [62].

CO₂ enters the surface ocean by diffusion and dissolution processes followed by a series of reactions leading to the formation of bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions (collectively, dissolved CO₂, bicarbonate and carbonate ions are designated as dissolved inorganic carbon, DIC):



The approximate ratio between the dissolved CO₂, bicarbonate, and carbonate ions in the ocean is (CO₂)_{aq}:(HCO₃⁻)_{aq}:(CO₃²⁻)_{aq} ≈ 1:100:10 [6]. The addition of CO₂ to seawater results in an increase in the (HCO₃⁻)_{aq} concentration and the ocean acidity. The ocean surface waters have slight alkalinity (pH 7.9–8.25), due to slow dissolution of minerals, which greatly facilitates the CO₂ uptake. Since the beginning

of industrial era, the pH of ocean surface water has decreased by 0.1 unit, which corresponds to a 26 % increase in hydrogen ion (H^+) concentration [15]. The lifetime of DIC in the surface ocean, relative to the exchange with the atmosphere and the deep and intermediate ocean layers, is less than a decade [6].

2.4.1.2 Terrestrial Carbon Cycle

In terrestrial biosphere, carbon is released (as CO_2) via two main routes: plant and animal respiration and detritus food chain (i.e., decomposition of organic matter). The carbon flux between the biosphere (which includes vegetation, soil, and detritus) and the atmosphere is estimated at 120 GtC/year (averaged over long periods of time). About 1 GtC/year is transported from land to the ocean by rivers in the form of DIC or suspended particles [6]. Other natural carbon fluxes include rock weathering, sediment accumulation, volcanic activity, and conversion of terrestrial organic matter into inert forms of carbon in soils. These carbon fluxes when averaged over decades do not exceed about 0.1 GtC/year [6]. According to Smith et al., the feedback between the terrestrial carbon cycle and climate will be one of the key determinants of the dynamics of the Earth system over the coming decades and centuries [63].

2.4.2 Interaction Between Carbon Cycle and Climate System

Available data indicate that there are multiple interactions between the Earth's natural carbon cycle and its climate system via a variety of mechanisms involving complex physical, chemical, photochemical, biological, and biogeochemical processes that, in many cases, are not adequately quantified or even understood. In particular, such components of the carbon cycle as the ocean, biosphere, and human activities can affect the GHG concentration in the atmosphere and, thus, indirectly influence the climate system. For example, biomass (vegetation) takes up CO_2 from the atmosphere during its growth and stores it in the form of carbohydrates, thus, diminishing the heat-trapping effect of CO_2 and its impact on climate. On the other hand, human activities cause CO_2 levels in the atmosphere to increase (e.g., via burning fossil fuels, cement manufacturing, land-use changes), thus, amplifying the greenhouse effect and warming of the climate.

2.5 Impact of Human Activities on Carbon Cycle

Throughout history, humans have been modifying their surroundings, and the magnitude of the modifications has risen with the growth of population and the improvement in the standard of living. Rapid growth of human population, especially during last two centuries, was fueled by the increasingly aggressive extraction and consumption of natural resources, which are energy and land intensive activities.

2.5.1 *Human Activities and Carbon Cycle*

An increasing body of scientific evidence suggests that human activities are affecting radiative forcing factors and carbon cycle [6, 64]. Impacts of human activities on carbon cycle are mainly attributed to the increased emissions of fossil-derived GHG (predominantly, CO₂) through industrial activity (e.g., power generation, cement manufacturing), land-use change, deforestation: all these practices became prevalent during the rapid industrial development of the past two and half centuries.

Although CO₂ as a main GHG of concern could come from different sources, there are many lines of the evidence that recent drastic increases in CO₂ emissions have humans' fingerprints [64, 65] (see also Sect. 2.2.1). Besides CO₂, humans are responsible for the recent growth in emissions of other potent GHG such as methane, nitrous oxide, and halocarbons (HC). For example, man-made methane emissions to the atmosphere (mostly, from agricultural practices: livestock farming, rice cultivation) account for nearly 70 % of annual methane emissions [64]. The concentration of nitrous oxide in the atmosphere has increased from preindustrial levels of about 270–319 ppb in 2005, primarily due to fuel burning at high temperatures [6].

Human activities impact the global carbon cycle by causing changes in the following two main carbon fluxes to the atmosphere [6]:

- CO₂ originating from combustion of fossil fuels and cement manufacture (about 80 % of total).
- CO₂ flux related to the land use changes (e.g., deforestation, agricultural development) (remaining 20 % of the total)

Cumulatively, CO₂ emissions due to global fossil fuel burning and cement manufacturing have increased by 70 % over the last three decades and reached 9.5 GtC² in 2011 [15]. In the land-use changes category, CO₂ emissions are estimated at 0.5–2.7 GtC per year range, summarily contributing to 6–39 % of the carbon emission growth rate, which is an equivalent of increasing total atmospheric CO₂ concentration by 12–35 ppm from the preindustrial period to the year 2000 [66]. Tropical deforestation is a main contributor to the increase in CO₂ flux to the atmosphere due to the land-use change.

Although the carbon fluxes caused by human activities constitute only a small fraction of the gross natural carbon fluxes (which constitute hundreds billion tons) within the atmosphere–ocean–land system, they still are responsible for the appreciable changes in the major carbon reservoirs compared to the preindustrial period (because the land and ocean cannot absorb all of the extra CO₂, but only part of it). From 1750 to 2011, CO₂ emissions to the atmosphere from fossil fuel combustion and cement manufacturing were 365 GtC, while the land-use change (including deforestation) was responsible for 180 GtC emissions (cumulatively from all sources, 545 GtC) [15]. Of these 545 GtC anthropogenic emissions, 240 GtC

²In this book, the amount of CO₂ may be presented in the units of carbon (C) or CO₂. For example, 1 GtC is equivalent of 3.66 GtCO₂.

(44.0 %) have accumulated in the atmosphere, 155 GtC (28.4 %) have been absorbed by the ocean, and 150 GtC (27.6 %) have been taken up by natural terrestrial ecosystems [15].

Thus, depending on the specifics of the carbon reservoir, human-induced carbon fluxes might cause certain perturbations to the natural carbon cycle. For example, in the ocean carbon reservoir, the biological pump might not directly absorb and store anthropogenic carbon, but rather do it through marine biological cycling of carbon facilitated by the increased atmospheric CO_2 concentrations [6]. Once becoming part of the global carbon cycle, anthropogenic CO_2 will be absorbed by ocean with the efficiency and the speed controlled by the rate of the movement of surface waters and their mixing with deeper ocean layers. It was estimated that about half of the amount of CO_2 added to the atmosphere will be removed via the carbon cycle within 30 years, and 20 % may stay in the atmosphere for thousands of years (and slowly neutralize by dissolved CaCO_3 from sediments) [43].

2.5.2 *Natural vs. Human-Induced Climate Drivers*

Climate is usually defined in terms of average temperature, precipitation, and wind over period of time, typically, 30 years [6]. It has long been recognized that the Earth's climate is controlled by the Sun's radiation and a variety of physical phenomena involving the Earth's atmosphere and surface such as absorption, reflection, dissipation, and emission of radiant energy. The climate system itself is a complex multifaceted system that is constantly changing governed by its own internal dynamics and a number of external factors such as variations in solar irradiance, and myriad interactions between atmosphere, land surface, oceans and seas, snow and glaciers, deserts, and terrestrial biosphere.

As discussed in Sect. 2.1, the radiation balance on the Earth's surface is fundamentally governed by three main factors [6]:

- Incoming solar radiation
- The fraction of reflected solar radiation (i.e., its albedo)
- The fraction of long wavelength radiation from the Earth back to space

Some of these factors (e.g., incoming solar radiation) are controlled exclusively by natural drivers, whereas the second and third factors could be influenced by both natural and anthropogenic drivers.

2.5.2.1 *Natural Drivers*

It is widely recognized that the variations in incoming solar radiation are due to the so-called *planetary* or *orbital forcing*, which is caused by the eccentricity, axial tilt, and precession of the Earth's orbit in relation to the Sun (the theory has been developed by James Croll and Milutin Milankovitch in the early twentieth century) [67]. The eccentricity (or ellipticity) of the Earth's orbit varies from 0 to 5 % on a cycle

of roughly 100,000 years, while its axial tilt varies from about 21.4° to 24.5° on a roughly 41,000-year cycle (currently, the axial tilt is 23.5°) [64]. Slight changes in these parameters could directly impact the amount of solar radiation reaching the Earth and, it is widely acknowledged that they drive historic glacial–interglacial climate variations (the so-called, *Milankovitch cycles*). Evidence from deep-sea sediments and ice cores suggests that considerable climate variability is associated with orbital forcing [68].

The changes in sunspots could also cause the variations in solar flux intensity and, hence, changes in climate [69]. Long-term observations indicate that the number of sunspots varies on a roughly 11-year cycle, which could potentially alter solar radiation intensity output by about 0.01 %. The available data suggest that during last two and half centuries, increased solar irradiance has contributed to an increase in positive RF of 0.06–0.30 W/m² [6]. Although this change is sufficient to contribute to moderate increase in temperature in the upper atmosphere, it cannot account for most of the observed increases in the Earth’s surface temperature [64].

The second factor (changes in albedo) is linked to the changes in terrestrial ecosystems (e.g., vegetation), or ice/snow cover, or a cloud cover, or presence of atmospheric aerosols, etc. Natural drivers include volcanic eruptions that emit immense quantities of aerosols (i.e., suspensions of microscopic and submicroscopic solid particles in air), sulfur gases (mainly, SO_x), and CO₂ into the atmosphere. Ash aerosols and sulfur gases reach stratosphere and can contribute to global cooling by reflecting and scattering incoming solar radiation back to space. Although volcanic ash is rather quickly removed from the atmosphere (typically, within a month after the eruption by sedimentation), sulfur gases stay much longer and are largely responsible for the climatic effects associated with the volcanic eruptions (sulfur gases from volcanoes make up about 36 % of the annual tropospheric sulfur emissions) [64, 70]. Natural variations in the Earth’s albedo could also result from changes in land and cloud cover, since it could directly affect the amount of solar radiation reflected or absorbed by the Earth’s surface and, thus, impact climate patterns. Increased cloud or snow cover can increase reflectance and provide cooling effect, whereas increased vegetation results in increased absorption of radiation, thus, providing warming effect (via the so-called *vegetative forcing*).

The third factor deals with the fraction of long wavelength radiation from the Earth back to space, which is affected by the atmospheric concentration of GHG. The examples of natural GHG sources include volcanoes releasing immense volumes of CO₂ during eruption, or various natural CO₂ vents, plant respiration, methane from permafrost, biogas (mixture of CH₄ and CO₂) from anaerobic digestion, plant decay, and weatherization of carbonate rocks. The magnitude of these emissions varies in a wide range (e.g., the amount of volcanic CO₂ is less than 1 % of annual total CO₂ emissions [71]).

2.5.2.2 Anthropogenic Drivers

Human activities contribute to the changes in the climate system by perturbing the fine balance between incoming/reflected solar radiation and outgoing infrared radiation due to alterations in the amount of GHG, aerosols, and cloudiness in the Earth's atmosphere. The changes in the Earth's albedo could be caused by such anthropogenic drivers as the release of ash aerosols and sulfur gases from coal-fired power plants, burning of vegetation, land surface change, urbanization, and release of GHG, etc. Each of these drivers has a complex and sometimes unpredictable impact on the albedo. Man-made aerosols have a different chemical composition (depending on the source), causing them differently interact with the atmosphere and affect the Earth's albedo (exerting cooling or warming effect). Aerosols (including black carbon particles) and sulfur gases produced from fossil fuel combustion and the burning of vegetation are the primary sources of man-made aerosols. Although anthropogenic aerosol emissions have declined in North America and Europe due to more stringent regulations, their level has increased in Asia (predominantly, China and India) with the dramatic rise in urbanization [64].

The increase in man-made GHG emissions and their accumulation in the atmosphere directly impacts the balance of long-wavelength radiation between the Earth and space. Although the increase in GHG levels in the atmosphere could be attributed to both natural and anthropogenic drivers, one should take into consideration that most of the natural sources existed for millions of years and, to a large extent, are responsible for the levels of GHG currently existing in the atmosphere. With the beginning of the Industrial Revolution in the mid-eighteenth century, a human factor started playing an increasingly bigger role in the growth of GHG emissions to the atmosphere and its impact on global carbon cycle and climate system.

Humans have also been altering the Earth's albedo via widespread transformation of land surface. It was estimated that humans have transformed or degraded between 39 and 50 % of Earth's surface (via population growth, development of necessary resources, etc.) [72]. Land surface change was mostly carried out through deforestation, reforestation, and urbanization, which substantially affected the Earth's albedo [64]. The reports show that the impact of land surface transformation on the Earth's albedo accounts for a loss of $RF = 0.4 \text{ W/m}^2$, thus, affecting the energy balance of the Earth's surface [6].

CO_2 flows between ocean and biosphere in the natural "breathing" of our planet, but the uptake of added man-made emissions depends on the net change between these flows that occur over decades to centuries to millennia [73]. According to many climate scientists, this implies that the climate changes caused by CO_2 will most likely persist for many centuries even if emissions were to be stopped at any point in time. Such an extreme "persistence" is unique to CO_2 among major GHG and warming agents. Emissions of such agents as black carbon, aerosols, methane, and ozone can potentially affect climate change over a period of years and decades, but

they exert relatively little impact on the Earth's climate over centuries. CO₂, on the other hand, is a much more persistent agent, and, as such, it primarily controls long-term impacts on climate.

2.5.3 Role of Feedback Mechanisms

The Earth's climate system is very sensitive not only to radiative energy balance variations but also to the changes in GHG in the atmosphere, and it could react via a variety of direct and indirect *feedback mechanisms*. The feedback mechanism could be of positive or negative nature, depending on whether it amplifies or negates, respectively, the effect of the change. The positive feedback (or "*feedback loops*") is of a particular concern, because it could easily lead to "runaway" situations. There are several types of feedback mechanisms, most important ones are discussed below.

2.5.3.1 CO₂–Water Vapor Feedback

One of the most significant feedback effects relate to a CO₂–water vapor feedback loop. According to this feedback mechanism, the water vapor level in the atmosphere is increased in response to rising concentration of atmospheric CO₂ and resulting GHG effect-induced warming. This, in turn, will cause additional CO₂ flux from the ocean to the atmosphere, thus, further intensifying the warming and further increasing water vapor concentration, and so on. It was reported that the effect of the CO₂–water vapor feedback loop could double the intensity of greenhouse effect compared to CO₂ acting alone [6]. Indeed, the reported data show that global precipitation has increased by about 2 % in response to the higher evaporation rates of the ocean waters during the twentieth century [64]. The magnitude of rainfall events has noticeably increased in many areas of the Northern Hemisphere and Australia. This trend, however, is contrasted with the decreased precipitation and increased aridity at low latitudes, e.g., northern Africa and Asia (which indicates that climate shifts will not be uniform). To some extent, the observed variability in precipitation patterns could be attributed to the El Niño Southern Oscillation (warm ocean currents and associated atmosphere influencing continental climate in many regions of the world).

2.5.3.2 Ice-Albedo Feedback

Another important example of a potentially powerful positive feedback mechanism relates to a so-called *ice-albedo feedback* [6]. The mechanism functions as follows: the rising levels of GHG in the atmosphere trap increasingly more heat and make the Earth's atmosphere warmer causing snow, glaciers, and polar ice caps (that reflect sunlight back to space) to melt. This would result in exposing increasingly

broader areas with the “dark” land and ocean surfaces that much better absorb solar heat than snow-covered surfaces. The resulting increase in the atmosphere temperature would melt more snow and ice, and so on. The consequence of this positive feedback could be an uncontrolled increase in temperature on the Earth’s surface in response to relatively low (in an absolute value) increase in GHG atmospheric concentration.

The dramatic shrinking of sea ice in the Arctic in recent summers was quite unexpected, because it was not predicted by many climate models [46]. In Antarctica and Greenland, large ice shelves are collapsing: warmer ocean waters are melting away the ice from below, while warmer air is opening cracks from above. Ice loss is feared not just because of ice-albedo feedback but also because of sea-level rise: although the loss of floating ice does not rise sea levels, the submerging glaciers do. Recent reports by glaciologists confirmed that ice losses from Greenland and West Antarctica have been accelerating, showing that some ice sheets are disconcertingly sensitive to climate change [74]. A current annual loss of 344 billion tons of glacial ice accounts for 20 % of current sea level rise (Greenland and West Antarctica have lost, respectively, 263 and 81 billion tons of ice per year from 2005 to 2010). Glaciologists are particularly concerned about the acceleration of losses, which shows that the glaciers are very sensitive to the changes in temperature.

2.5.3.3 Ocean Current Feedback

The most rapid of the feedback mechanisms involves the ocean currents that carry heat around our planet. In warmer climate, collapsing glaciers and/or increased precipitation could dump a massive amount of freshwater into the northern seas causing warm currents to slow down or completely stop, and, as a result, disrupting the engine that drives global ocean currents and, thus, causing more warming [46]. If fully realized, the impact of this feedback might appear very quickly, e.g., Greenland could turn from cool to warm within a decade or so. The rate of adding freshwater is a critical parameter here, and some studies suggest that, fortunately, at the present rate freshwater is not added fast enough to fundamentally alter climate.

Another possible source of the ocean current feedback is located in much warmer areas of our planet. It has been reported that warming waters in the Gulf Stream (that transports warm waters from the Gulf of Mexico into the North Atlantic ocean) can potentially thaw and destabilize hundreds of gigatons of methane hydrates trapped below the seafloor, increasing the risk of the slope failure and methane release into the atmosphere [75]. Additionally, slight changes in the Gulf Stream flow direction can also destabilize methane hydrate by redirecting warm waters to regions previously exposed only to cold bottom currents. The Gulf Stream consists of anomalously warm water at the depths as great as 1,000 m below sea level; at the intermediate water depths of 300–1,000 m, the Gulf Stream temperature is 8 ± 1.1 °C warmer than ocean temperatures outside the current [75]. The destabilization of methane hydrates could extend along hundreds of kilometers of the western North Atlantic margin, it may continue for centuries and release approximately 2.5 Gt of methane (about 0.2 % of the amount of methane hydrates required to cause such

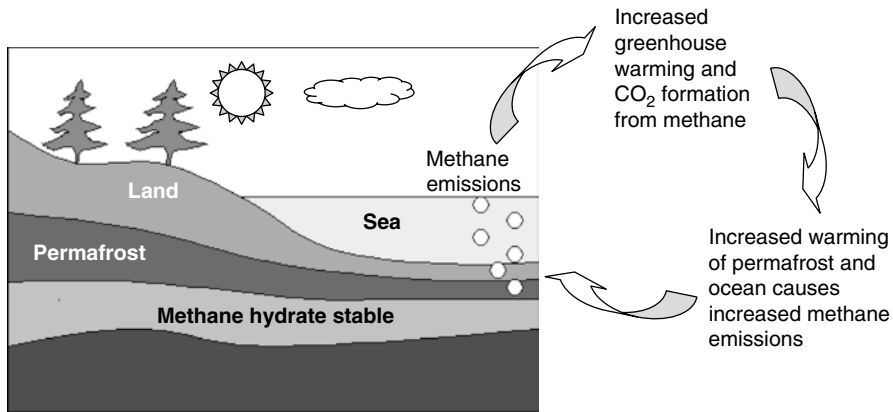


Fig. 2.10 The schematic of a positive methane-induced feedback mechanism. *Source* [35]

catastrophic event as PETM). (The authors of the study note that there could be other areas experiencing changing ocean current; thus, the quantity of destabilized methane hydrates could be much greater.) If most of the released methane will find its way to the atmosphere, this could potentially trigger the feedback loop, however, the prospect of this event and, consequently, its impact on climate still remains uncertain [76].

2.5.3.4 Permafrost Feedback

A more immediate feedback that is already manifesting itself in several locations worldwide involves permafrost (see also Sect. 2.3.3.2). It was not until recently that scientists realized the scale of the potentially devastating impact of the permafrost feedback. Permafrost stores hundreds of billions of tons of methane, roughly double the amount of carbon in the atmosphere [46]. Siberia (Russia) is dotted with giant hills of organic-rich permafrost. There are two types of feedback mechanisms that could result in accelerating release of methane from permafrost in a response to climate change. According to the first (biological) route, in warming climate, more thawing stimulates microbial anaerobic digestion of organic carbon with production of two potent GHG: methane and CO₂. In another feedback mechanism, methane hydrates that occur within or beneath thick terrestrial permafrost may begin to dissociate with the release of methane as surface temperature increases. Pronounced regional warming increases methane emissions from permafrost and destabilized methane hydrates, which strengthens the greenhouse effect (directly by methane and indirectly by CO₂ generated by methane oxidation in the atmosphere) and further warms the surface [21]. This warming, in turn, triggers the additional methane emissions via an auto-accelerating cyclic mechanism. Figure 2.10 depicts the scheme of a positive methane-induced feedback mechanism.

There are multiple observations of methane bubbling up from the shallow lake bottoms formed by melting permafrost. It was found that permafrost could crack open into the so-called thermokarsts (mini canyons), which facilitates melting and the release of GHG (see also Fig. 2.7). Recent expeditions in Arctic regions, e.g., off Spitsbergen, Norway, and Siberia, have detected plumes of methane rising from the shallow waters [46].

There is also another potentially significant cause of methane feedback: tropical wetlands, which present the predominant natural source of methane. As the atmosphere warms, rainfall increases in the tropics, and, consequently, the wetlands expand and become more productive, which creates more anaerobic digestion with the release of methane and CO₂. According to estimates, expanded wetlands could release as much additional methane as that from Arctic warming [46].

2.5.3.5 Ecological Feedback

Ecological feedback mechanism involves changes in the Earth's ecosystem in response to warming climate. For example, warmer temperatures in the northwestern USA and western Canada have triggered an epidemic of mountain pine beetles. The insects destroyed hundreds of thousands of hectares of trees, threatening to turn forests from carbon sinks into carbon sources (due to decomposition of dead trees) [46]. Another example of the ecological feedback: warming in Siberia is starting to transform vast forests of larches into spruce and fir woodlands. This change could markedly affect radiative balance as follows: larches drop their leaves in winter, thereby allowing solar radiation to reflect off the snow cover, whereas spruces and firs keep their needles, thus, absorbing solar heat and minimizing light reflection from snow. Feedback from vegetation changes alone could warm the planet by about 1.5 °C [46].

2.5.3.6 Cloud Feedback

Cloud feedback is an example of the feedback mechanism that could be both negative and positive, and it relates to clouds, which play an important role in regulating the Earth's climate. On the one hand, clouds are effective absorbers of long wavelength radiation, and, as such, amplify the greenhouse effect (i.e., via the positive feedback mechanism since more clouds would result in the more pronounced greenhouse effect and the Earth surface warming). On the other hand, clouds also very effectively reflect solar radiation, thus, potentially causing a negative feedback effect, since more clouds result in more reflection and cooling the Earth. Even minor changes in clouds' consistency and location could cause either a positive or negative feedback effect.

Summarizing, the climate feedback phenomenon and its implications are of vital importance to the very survival of humankind; therefore, this issue is at the center of intensive worldwide research efforts. Although climate experts may not agree on

the pace of climate change, there is a realization that specific feedback mechanisms might already be working and amplifying the change, and this causes a profound concern about our planet's future. Climate models, although good at explaining the past and present climatic events, are still unsatisfactory in predicting potential future impacts of various feedback loops. To put it simply: "*scientists know the direction, but not the rate*" [46]. Yet the scientists agree that uncertainties do not justify inaction; on the contrary, they call for the immediate worldwide efforts to reduce GHG emissions, which are one of the main factors triggering feedback loops.

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Liberating Energy from Carbon: Introduction to
Decarbonization

Muradov, N.

2014, XXIV, 433 p. 86 illus., 34 illus. in color., Hardcover

ISBN: 978-1-4939-0544-7