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Preface

This is the era of global warming with the associated climate change, and increase in the frequency of extreme events. Beginning with the Industrial Revolution since circa 1750, the atmospheric concentration of heat-trapping greenhouse gases (GHGs) has increased significantly as a result of anthropogenic activities. Three major GHGs and their current atmospheric abundance relative to Industrial Era circa 1750 are carbon dioxide (CO_2) 145%, methane (CH_4) 254%, and nitrous oxide (N_2O) 121%. Other human-created GHGs are sulfur hexafluoride (SF_6), and many halogenated species. Emission of GHGs to the atmosphere is of a primary concern worldwide because the radiative properties of the atmosphere are strongly impacted by their abundance in the atmosphere. These gases have sometimes been referred to as well-mixed or long-lived GHGs because they are sufficiently mixed in the troposphere such that concentration measurements from few remote surface sites can characterize their atmospheric burden and their atmospheric lifetimes are much greater than timescales of few years of atmospheric mixing.

The Earth′s climate is determined by the flows of energy into and out of the planet and to and from the Earth's surface. Increasing GHGs in the atmosphere therefore, creates imbalance in energy flows in and out of the Earth system by trapping more radiation energy. Trapped energy is manifested in many ways, including rising global surface temperatures, melting Arctic sea ice, accelerating the water cycle, altering the intensity and frequency of storms, and many more changes. In addition to impact on global climate, CO_2 also interact strongly with the biosphere and oceans. The atmospheric content of these gases also represent gaseous phase of the global biogeochemical cycles that control the flows and transformation of C and N between the different compartments of the Earth system, namely atmosphere, biosphere, hydrosphere, and lithosphere, by both biotic and abiotic processes. The increase in atmospheric CO_2 concentration is the main driver of the anthropogenic climate change, accounting for 1.939 of 2.974 W m^2 or 65% of the global-radiative forcing between 1750 and 2015. From 1990 to 2015, the radiative forcing by the long-lived GHGs increased by 37.4% with CO_2 accounting for about 80% of this increase. The two major sources of CO_2 emission are fossil fuel combustion and land use conversion. As a result of increase in anthropogenic emission of GHGs, the global annual mean land and ocean temperature increased by about 1.11 °C between 1750 and 2015, accompanied by the worldwide melting of glaciers and rising of the sea level.

Whereas the land use conversion was the major source of atmospheric CO_2 emissions ever since the dawn of settled agriculture, fossil fuel combustion has been increasingly important since the Industrial Revolution that began circa 1750. Presently, energy production and the environment are the two most important challenges facing the humanity in the twenty-first century. More than 80% of the energy comes from the fossil fuel combustion, and fossil fuels will remain the dominant energy source for years to come. Emission of CO_2 from the fossil fuel combustion process is the dominant anthropogenic GHG causing climate change because burning fossil fuels releases the CO_2 to the atmosphere that was stored millions of years ago, and thus, was unavailable for C cycling. Therefore, fossil fuels combustion transfers large quantities of C from slow domain C cycling to fast domain C cycling. Fossil fuel combustion accounts for about 75% of anthropogenic CO_2 emissions and is expected to further increase by 53 to 55%, while meeting 83% of the increase in energy demand by 2030. Prompt global action to resolve CO_2 emission crisis is needed in the short term, and the need to move away from C economy in longer term. In addition to energy conservation, C sequestration is one of an alternative method to reduce the rate of atmospheric CO_2 increase and mitigate climate change.

Global climate change presents a unique challenge to mankind, which requires a joint global effort to address. Whether global governments and public will act sufficiently fast to stabilize the global temperature at an acceptable levels and avoid dangerous impact remains the most uncertain proposition. For the policy makers, regulating fossil fuel use to the levels that will avoid dangerous warming is most difficult task because fossil fuel use has direct impact on economic prosperity. To the experts in physics, climate scientists, and others, the physics of radiation and energy balance, together with ocean circulation and Earth's long climate history, the global warming evidence is compelling.

Carbon (C) sequestration is the process of transferring atmospheric CO_2 that would otherwise be emitted into and/or remain in the atmosphere, and securely storing it in other long-lived C pools or protecting C that is stored in long-term pool that would otherwise be emitted, either through natural biological, enhanced natural biological processes, or anthropogenically driven non-biological engineering techniques. It aims at prevention of CO_2 from emission into atmosphere or transferring C from the atmosphere into long-lived pools—including biota, soil, geologic strata, and ocean. Strategies for C sequestration can be grouped into biotic and abiotic. Biotic strategies utilize ecological process of photosynthesis and transfer of CO_2 from atmosphere into plant biomass C through mediation of green plants, followed by utilization of biomass to substitute for fossil fuels or use of wood to substitute cement in construction. Biomass also can enhance soil organic C (SOC) storage, transferred to pedologic storage through OM burial and transformation into fossil C. Ocean CO_2 fixation also occurs through photosynthesis, followed by OM burial in deep ocean sediments. Abiotic strategies involve separation, capture, and storage of CO_2 into geologic strata using geoengineered processes which keeps industrial CO_2 emissions from reaching the atmosphere. The overall objective of the C sequestration—both biological and anthropogenic—is to balance the global C budget such that the current and future economic growth is based on C neutral or C negative strategy where there is either no net CO_2 emission or net negative CO_2 emission.

The *Carbon Sequestration and Climate Change Mitigation and Adaptation* book sets out a scientific basis of the current understanding of the role of increased CO_2 emission on climate change. The book explores an extensive field of current scientific knowledge that includes the general science of Earth's climate, how and why climate is changing, and consequences of those changes to food security and prosperity. The paleoclimatological studies form the basis of distinguishing between natural and anthropogenic climate change. The book also describes the role of C sequestration—both ecological engineered and geoengineed options—for mitigating the increasing atmospheric CO_2 concentration. In addition, the role of a proposed and emerging climate engineering and chemical sequestration option is briefly examined with the emphasis on their limitations and possible risks. Information from different scientific disciplines is collated and integrated to present a holistic approach towards the role of CO_2 and other GHGs on global warming, climate change, and the approaches for mitigating climate change and its impacts. The book is specifically prepared to provide academic and research knowledge for undergraduate and graduate university students, scientists, researchers, and policy makers interested in general understanding of the anthropogenic CO_2 emissions and its impact on global C cycling and C budgets, approaches for reducing CO_2 emissions, and available options for mitigating global warming.

We thank Springer Dordrecht and the Life Sciences staff for extending the opportunity to publish with them and share this knowledge. Particularly, we are indebted to Melanie van Overbeek and the staff of the Agronomy for their patience and tireless guide which allowed the completion of this task.

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Chapter 1
Introduction: Climate Overview

Abstract Energy exchange between Sun, Earth, and space controls the global climate. Earth is in dynamic equilibrium such that it receives the radiation from the Sun and emits the same amount of heat as infrared (IR) energy to space. Earth's energy imbalance is the difference between the incoming solar radiation absorbed by the Earth and the amount of heat the Earth radiates to the space. If positive imbalance occurs, such that the incoming radiation from the Sun is more than outgoing heat from the Earth, Earth becomes warmer. In contrast, if the imbalance is negative, such that more energy is going out than it receives, then Earth will cool. Earth's energy imbalance is the single most important measure of the status of the Earth's climate system which defines the expectations of future global climate change resulting from the anthropogenic perturbation or the greenhouse effect. The energy budget of the Earth's climate system is discussed in this chapter. The processes that Earth retains more electromagnetic radiation energy than it receives are also explained. In addition, the role of greenhouse gases (GHGs) in regulating the energy balance is discussed with the emphasis on carbon dioxide (CO_2). The concentrations of GHGs have increased significantly since the Industrial Revolution $\sim$ circa 1750. Most notable is the increase in concentration of CO_2 which have played a significant role in the current and future global temperature increases.

Keywords Climate system · Infrared radiation · Greenhouse gases · Ultraviolet radiation · Energy budget · Global warming

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1.1 Weather and Climate

Weather is the physical condition or state of the atmosphere at a certain places at a given time with reference to meteorological elements. It is what is happening in the atmosphere at any time or over any short period of time. The principal meteorological elements which defines the weather are: temperature, pressure, precipitation, wind, moisture, humidity, and other key parameters of meteorological importance such as presence of clouds, and occurrence of special phenomena such as thunderstorms, dust storms, tornados, and others. Therefore, the large fluctuations in the atmosphere from hour to hour or day to day constitute weather. These fluctuations occur as the weather system moves, develops, evolves, matures, and decays as a form of atmospheric turbulence. The weather systems arise mostly from atmospheric instabilities which are nonlinear chaotic dynamics such that they are not predictable in the individual deterministic sense beyond a week or so in the future. Meteorologists put a great deal of effort into understanding and predicting these day-to-day evolution of weather systems, and using physical based concepts that govern changes in atmosphere, they are able to predict the weather successfully only beyond several days into the future due to fundamental dynamical properties of the atmosphere.

According to Intergovernmental Panel on Climate Change (IPCC 2001, 2007) climate is generally defined as the average weather at a given period of time and space. It is described in terms of statistical quantities of mean and variability of surface weather variables over a period of time ranging from months to thousands or millions of years, and possibly over a certain geographical region. Climate description includes mean condition and the associated statistics such as frequency, magnitude, persistence trends, etc., often combining these statistical parameters to describe phenomena such as droughts. The classical period which has been adopted by World Meteorological Organization (WMO) for averaging these variables is 30 years. Temperature, precipitation, and wind are the most commonly used quantities to describe climate and to classify it into specific categories assigned to different parts of the world. Therefore, climate in a wider sense is an average state of the atmosphere observed as the weather over a finite period such as season for a number of different years. Climate is described in terms of mean and variability of weather elements such as temperature, precipitation, and wind over a specified time. It can range from months to millions of years. Climate comprises a variety of space and timescales from diurnal cycle to inter-annual variability such as El-Nino Sothern Oscillation (ENSO) to multi-decadal variations. There is no such thing as global weather but there is a global climate. Climate system is a complex relative system which involves the status of the entire Earth system, including atmosphere, land, oceans, snow, ice, living things that serves as the background conditions that determines weather patterns. Climate varies from place to place depending on latitude distance, distance to the ocean, vegetation, presence or absence of mountains, or other geographical factors. Climate also varies in time, from season to season, year to year, decade to decade or much longer timescales such as Ice Ages. The statistically significant variations of the mean state of climate or its variability that can be identified using statistical tests by change in mean and/or variability of properties persisting for extended periods, typically decades or longer are referred to as climate change. Although many other factors continues to influence the climate, human activities have become a dominant force and are responsible for most of warming observed in the past 50 years.

Traditionally, weather and climate focuses on those variables that affect daily life most directly—such as average, minimum and maximum temperature, wind near the surface of the Earth, precipitation in different forms, humidity, cloud type and amount, solar radiation—which are observed hourly by a large number of weather stations. But this is only part of reality that determines weather and climate. The climate of the Earth depends on factors that influence the radiative balance such as atmospheric composition, solar radiation or volcanic eruptions (Baede et al. 2001).

1.2 Solar Radiation and Climate

The amount and distribution of incoming radiation from the Sun determines weather and climate on the Earth (Trenberth et al. 2009). Therefore, solar radiation provides nearly all the energy that drives global climate system, and approximately half of the energy from the Sun is supplied by the visible part of electromagnetic spectrum. Solar energy leaves the Sun as electromagnetic radiation and travels through the space and atmosphere to reach the Earth's surface. Electromagnetic waves (also called electromagnetic radiation) are produced by the motion of electrically charged particles. The electromagnetic spectrum consists of light varying from long wavelength (low energy) to very short wavelength (very high energy). The solar radiation reaching the top of the atmosphere is (a) partially transferred, (b) partially transformed into other forms of energy which are dissipated by general circulations of the atmosphere and oceans, and (c) partially used in chemical and biological processes.

Within the climate system, energy occurs in different types including heat, potential energy, kinetic energy, chemical energy, short wave and long wave radiations. The climate system can therefore be described as weather generating heat engine driven by the solar radiation energy input and thermal radiation output (Peixoto and Oort 1992). The Sun emits radiation over a spectrum of energies that exist in the form of waves; the radiation wavelength is the inverse of energy. On the high energy side of solar spectrum is ultraviolet (UV) and on the low energy side is infrared (IR) radiation. Although the solar radiation covers the entire electromagnetic spectrum from gamma rays and X-rays through microwaves and radio waves, about 99% of the electromagnetic radiation emitted by the Sun reaching the Earth has the wavelengths (λ) of 0.15–4.0 μm (i.e., 1 μm = 10^{-6} m), with 9% in UV ($\lambda < 0.4$ μm), 49% in the visible spectrum ($0.4 < \lambda < 0.7$ μm), and 42% in IR ($\lambda > 0.7$ μm) ranges. The balance between the solar energy that Earth receives from the Sun and that which it radiates out to the space is a major driver of the Earth's climate. Quantification of the amount of energy flow in and out of the Earth system and identification of the factors determining the balance between the incoming and outgoing energy helps in understanding the climate change.

1.2.1 Radiation Balance of Earth and Atmosphere

Although there are various atmosphere, ocean, and land phenomena that couple the energy balance, for the equilibrium climate over time, and absorbed shortwave solar radiation from Sun balances the outgoing long wave radiation from Earth. Variations in global energy balance affects thermal conditions on Earth and various other climate elements such as atmospheric and oceanic circulations, hydrological cycle, glacier dynamic, plant productivity and also terrestrial carbon (C) uptake (Ramanathan et al. 2001; Ohmura et al. 2007; Wild et al. 2008; Mercado et al. 2009). The knowledge of the energy exchange between Sun, Earth and space has been improved through new satellite missions—Cloud and Earth's Radiation Energy System (CERES, Wielicki et al. 1996) and Solar Radiation and Climate Experiment (SORCE, Anderson and Cahalan 2005; Kopp et al. 2005) which began acquiring data in 2000 and 2005, respectively (Wild et al. 2013). These have allowed determination of the radiative flux exchanges on the top of the atmosphere with higher accuracy than previously published records (Loeb et al. 2012a). The radiant energy that falls on a surface of one square meter in area outside the atmosphere directly facing the Sun during 2008 and recorded by Total Irradiance Monitor (TMI) is 1360.8 ± 0.5 W (Kopp and Lean 2011). This value is ~4.5 W m^{-2} lower than previously reported value, and the difference has been attributed to instrumental bias for the older measurements recorded by older instrumentation. The new more accurate record requires an updating of the energy budget to reflect these new measurements (Hartmann et al. 2013). Only few parts of Earth faces the Sun directly, and also half of the time half of the Earth is pointing away from the Sun at night. Therefore, the average solar irradiance falling on one square meter of the level surface at the top of atmosphere is only a quarter of this (i.e., the area of a sphere is four times the area of a disk), which corresponds to a global average solar radiation of 340 W m^{-2} averaged over the Earth's sphere (Hartmann et al. 2013). The radiation balance of Earth and atmosphere with the updated annual mean radiation balance for the climate system as a whole is presented in Fig. 1.1. It is separated into incoming solar radiation, outgoing radiation and different components of terrestrial radiation and energy budgets.

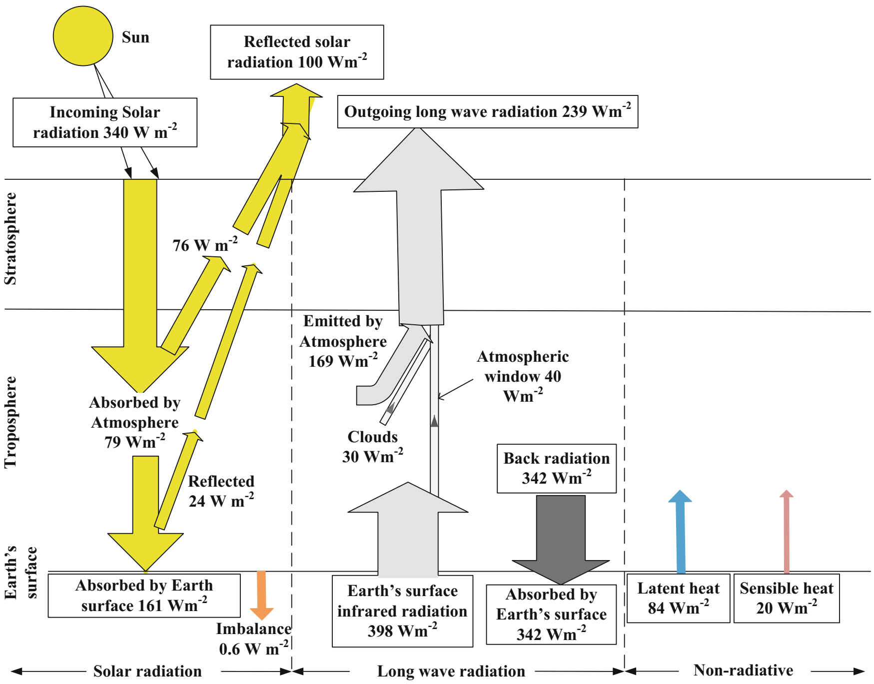

Fig. 1.1 Global mean energy balance of the Earth. *Numbers* and *text* in *box* indicate measured values, other *numbers* indicate best estimates for the magnitudes of globally averaged energy balance to close the balance. Adapted from Ussiri and Lal (2013), with an updated data from Wild et al. (2013), Hartmann et al. (2013)

As the solar radiation passes through the atmosphere, some of it is reflected back to the space by the atmospheric molecules. The total solar radiation reflected back to space measured at the top of the atmosphere is 100 W m^{-2} (Loeb et al. 2012b; Wild et al. 2013). Therefore, a total of 240 W m^{-2} (i.e., 340–100 W m^{-2}) of the solar radiation is available to the climate system. This radiant energy is either absorbed or reflected at the Earth's surface. It is also transformed into sensible heat, latent heat involving different water states, potential energy, and kinetic energy before being emitted as long wave radiant energy. Energy may be stored for a duration of time in various form and converted among different types of energy, which might produce varieties of weather or turbulent phenomena in the atmosphere and ocean (Trenberth et al. 2009).

The atmosphere is fairly transparent to short wavelength solar radiation. It is estimated that the atmosphere absorbs only about 80 W m^{-2} of the incoming solar radiation (Kim and Ramanathan 2008, 2012; Trenberth et al. 2009; Trenberth and Fasullo 2012; Wild et al. 2013; Kato et al. 2013). This leaves about 161 W m^{-2} to be transmitted and reach the Earth surface. Much less is known however about the energy distribution within the climate system and at the Earth's surface. The surface energy fluxes cannot be measured directly by the satellites as those at the top of the atmosphere (TOA), but they are inferred from the measurements at the TOA radiances using empirical calculations and physical modelling to account for the atmospheric attenuation (Wild et al. 2013). The downward thermal IR radiation at the surface established after incorporation of cloud base heights from the space-borne radar and lidar instruments is 342 W m^{-2} (range 338–348 W m^{-2}) (Fig. 1.1, Stephens et al. 2012b; Kato et al. 2013). This is the radiation emitted by GHGs and clouds, also known as back radiation. Additionally, direct surface radiation measurements from ground based radiation network of instrumentations propose similar values of downward thermal radiation (Wild et al. 2013). The land surface receives 185 W m^{-2} and absorbs about 161 W m^{-2} of the solar radiation, while reflecting an estimated 24 W m^{-2} back to space. Therefore, ~76 W m^{-2} of the solar radiation is directly reflected into space from the atmosphere (Fig. 1.1). The energy absorbed by the vegetation layer drives the plant processes such as evapotranspiration, photosynthesis, and C assimilation, while the remaining fraction available in the underlying soils controls evaporation on land and oceans, snow melting, and other temperature-related processes (Sellers et al. 1997).

To balance for this incoming energy, Earth itself must radiate the same amount of energy back to space in the form of thermal radiation. All objects emit this form of radiation, and if they are hot enough the emitted radiation falls in the visible spectrum. For example, the Sun is at the temperature of 6000 °C and looks white (shortwave radiation). Cooler objects emit radiation in the IR range (long wave radiation). The amount of thermal radiation emitted by the Earth's surface depends on its temperature, and how absorbing the surface is. The warmer the surface is, the more radiation is emitted, and also the greater the absorption, the more the radiation is emitted. All the surfaces on Earth absorb nearly all the thermal radiation which falls on them instead of reflecting it. The Earth radiates thermal energy equivalent to solar radiation energy received back. The solar flux energy intercepted per second by the Earth's surface can be expressed as Eq. (1.1):

$$F_s(1-A)\pi R_e^2 \tag{1.1}$$

where, F_s is the solar flux constant at the top of atmosphere (1360 W m^{-2}), R_e is the radius of the Earth (6.38×10^6 m), and A is the Earth's albedo, which correspond to reduction of incoming solar radiation flux by absorption and scattering of radiation by aerosol particle (average value = 0.28). Based on the temperature of the Earth's surface, the majority of outgoing energy flux from the Earth is in the longwave range of spectrum. This longwave radiation is also referred to as infrared (IR) radiation. The IR energy emitted per second from the Earth's surface (black body radiation) is expressed as Eq. (1.2):

$$4\pi R_e^2 s T_e^4 \tag{1.2}$$

where, s is Stephan-Boltzman constant (5.67×10^{-8} J $m^{-2} \times K^{-4}$), and $4\pi R_e^2$ is the surface area of the Earth. At equilibrium, the temperature of the Earth (T_e) is expressed as Eq. (1.3):

$$T_e = [F_s^*(1 - A)^* 1/4_s]^{1/4} \tag{1.3}$$

If the Earth was to emit thermal energy equivalent to solar radiation received back to space, temperature at the Earth surface will be around −19 °C (255 K) based on the energy balance requirements calculated using Eq. (1.3), which is the temperature observed at the altitude of 5–6 km above the Earth's surface (Peixoto and Oort 1992). However, an average of current temperatures measured near the surface across the globe over the land as well as over the oceans over the whole year indicates a global temperature of about 15 °C.

The Earth, being colder than the Sun, is warmed and it radiates heat as long waves (Fig. 1.1), primarily IR. The surface IR of 398 W m^{-2} (or about 114% of solar radiation from the Sun) corresponds to black body emission at 15 °C on Earth's surface, decreasing with altitude, and reaching mean temperature of −58 °C at the top of the atmosphere (i.e., troposphere, the layer closest to the Earth) about 15 km above the Earth's surface. The thermal radiation leaving the top of the atmosphere in the IR part of spectrum can be measured from instruments mounted on orbiting satellites. The outgoing thermal emission measured at the top of the atmosphere from 2005 to 2010 is 239 W m^{-2} (Hansen et al. 2011; Loeb et al. 2012b). Therefore, the heat radiation emitted by the surface (398 W m^{-2}) is greater than 239 W m^{-2} by the atmosphere by 159 W m^{-2}, which is the measure of greenhouse trapping. The global heat storage is estimated at 0.2–1.0 W m^{-2} (average = 0.6 W m^{-2}). This leaves 106 W m^{-2} of surface net radiation available globally for distribution among the non-radiative surface energy balance components—sensible heat, latent heat, and residual energy. Globally estimated sensible heat is estimated as 15–25 W m^{-2} (Trenberth et al. 2009; Stephens et al. 2012a). The estimates for global latent heat (i.e., energy equivalent of evaporation, globally equals precipitation) is estimated at 84 W m^{-2} (Trenberth and Fasullo 2012); but uncertainty remains higher due to variation in precipitation from year to year (Adler et al. 2012).

1.3 Greenhouse Effect

1.3.1 The Natural Greenhouse Effect

The gases nitrogen (N_2), oxygen (O_2) and argon (Ar) that make up the bulk of the atmosphere (Table 1.1) do not absorb or emit thermal radiation. If they were the only atmospheric components there would not be any clouds and no greenhouse effect, and to achieve radiative balance the average Earth's surface temperature

Table 1.1 The global average concentration of well mixed atmospheric constituents, their changes since industrial era and radiative efficiency (IPCC 2007, 2013; Schlesinger and Bernhardt 2013)

Gas	Radiative efficiency W m^{-2} ppb^{-1}	Mixing ratio			Global increase (2005–2011)
		1750	2005	2011	
Major constituents (%)					
Nitrogen (N_2)	0	78.084	78.084	78.084	–
Oxygen (O_2)	0	20.946	20.946	20.946	–
Argon (Ar)	0	0.934	0.934	0.934	–
Water vapor (H_2O)		0–0.02	0–0.02	0–0.02	–
Parts per million (ppm) constituents					
Carbon dioxide (CO_2)	1.37×10^{-5}	278 ± 2	379	390 ± 0.28	11.67 ± 0.37
Helium	0	5.24	5.24	5.24	5.24
Krypton	0	1.14	1.14	1.14	1.14
Parts per billion (ppb) constituents					
Methane (NH_4)	3.63×10^{-4}	722 ± 22	1774	1803 ± 4.8	28.9 ± 6.8
Nitrous oxide (N_2O)	3.00×10^{-3}	270 ± 7	319	324.0 ± 0.1	4.7 ± 0.2
Chlorofluorocarbons (parts per trillion)					
CFC-11	0.26	0	251	236.9 ± 0.1	−13.0 ± 0.1
CFC-12	0.32	0	542	539.5 ± 0.2	−14.1 ± 0.1
CFC-113	0.30	0	78.6	74.3 ± 0.06	−4.35 ± 0.02
CFC-115	0.20	0	8.36	8.37	–

would be −6 °C (Houghton 2005). The difference between this and the actual observed temperature is about 20 °C. Presence of trace gases, those which account for less than 1% of the total volume of dry air in the atmosphere, plays important role in Earths' energy budget by absorbing and re-emitting IR radiation emitted by Earth surface, preventing it from escaping to the space. Water vapor ($H_2O(g)$), CO_2, methane (CH_4), nitrous oxide (N_2O) are known as the trace gases because of their smaller quantities in the atmosphere, they are also called GHGs because they absorb some of the thermal radiation leaving the surface and emit long wave radiation into all directions, while acting as partial blanket and keeping the Earth warm. As a result, most of the radiant heat flows back and forth between Earth's surface and atmosphere, and absorbed in the atmosphere to keep the Earth's surface warm. The downward directed component of IR adds heat to the lower layers of the atmosphere and the Earth's surface causing the so called greenhouse effect. The dominant energy loss of IR radiation from the Earth occurs from higher layers of troposphere.

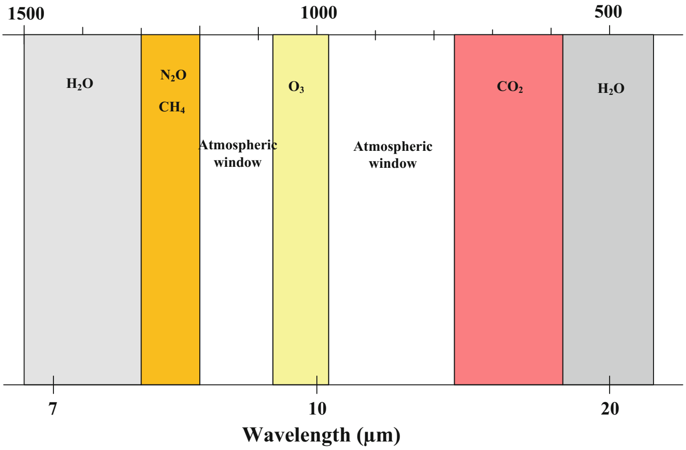

Fig. 1.2 Part of infrared spectrum (7–21 µm) showing locations where different gases contribute to the radiation. Between 8 and 14 µm, apart from O_3 in the absence of clouds is transparent to radiation, this part of the spectrum is called 'atmospheric window'. Modified from Houghton (2005)

Transfer of radiation in the atmosphere as seen by satellites orbiting the Earth is shown in Fig. 1.2. At some wavelengths (8–14 µm) in the IR the atmosphere in the absence of clouds is transparent, and almost all radiation originating from the Earth's surface leaves the atmosphere. All other wavelength radiation from the surface of the Earth is strongly absorbed by water vapor, CO_2, CH_4 and N_2O present in the atmosphere. Particularly water vapor and CO_2 are the strongest absorbers. Objects which are good absorbers of radiation are also good emitters of it.

The amount of radiation they emit depends on the temperature. At the top of atmosphere (5–10 km high) the temperature is much colder (30–50 °C colder than the surface) because of convection processes (Fig. 1.3). Because these gases are cold, they emit less radiation out to the space. They, therefore, act as a radiation blanket over the surface, and help to keep it warmer than it would otherwise be. This partial blanketing is known as natural greenhouse effect, and these gases are known as GHGs. This phenomenon is natural because these trace gases were present in the atmosphere even prior to any anthropogenic perturbation. The amount of water vapor present in the atmosphere is variable and mostly dependent on the surface temperature of the oceans, and most of it originates from the evaporation from the ocean surface and is not directly influenced by anthropogenic activities. The natural greenhouse effect is important in maintaining the Earth's climate with its suitability for life to flourish.

Clouds also play significant role in maintaining Earth's radiation balance (Fig. 1.1). Clouds reflect some of the incident radiation from the Sun back to space. They also absorb and emit thermal radiation and have a 'blanketing effect' similar to the trace gases. These two effects of clouds tends to cancel each other, leaving

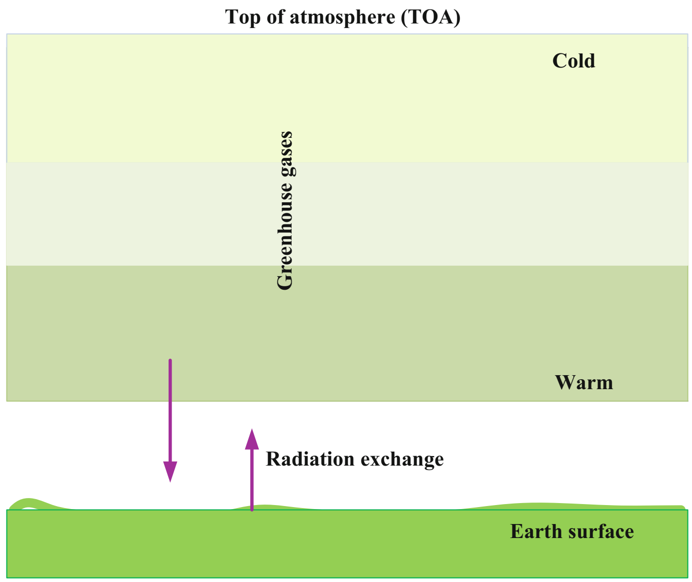

Fig. 1.3 Illustration of blanketing effect of greenhouse gases in the atmosphere

total radiation balance unchanged or slight cooling of the Earth's surface. Sun provides its energy to the Earth primarily in tropics and subtropics, and this energy is then partially redistributed to middle and high latitudes by atmospheric and oceanic transport processes, while the outgoing long wave radiation is more uniformly distributed with latitude (Fasullo and Trenberth 2008a, b).

1.3.2 Discovery of the Science of Greenhouse Effect

The warming effect of the GHGs in the atmosphere was first recognized by a French scientist Jean-Baptiste Fourier who pointed out the similarity between what happens in the atmosphere and inside the greenhouse in 1827. In 1838, Fourier and Claude Pouillet were able to measure the heating effects of radiation with mercury-in-glass (Mudge 1997). They observed that the atmosphere absorbs less of the incoming radiation than the outgoing radiation and suggested that this difference would account for the Earth remaining at the higher temperature than it would if there were no atmosphere. This is the origin of the name 'greenhouse effect'.

A British scientist John Tyndall considered the part played by the minor components of the atmosphere in producing remarkable temperature conditions of the mountainous country. To measure the intensity of heat directly, he designed and built the first infrared spectrometer. In 1860 he measured the absorption of infrared radiation by CO_2 and water vapor (H_2O) using this device. He was able to show that

O_2 and N_2 are almost completely transparent to heat and CO_2 and water vapor are powerful absorbers and radiators of heat. He also suggested that the cause of ice ages might have been the decrease in the greenhouse effect of CO_2. A Swedish chemist Svante Arrhenius calculated the effect of increasing concentration of GHGs in 1896 and estimated that doubling the concentration of CO_2 would increase the global average temperature by 5–6 °C. His estimates are not far from present understanding of 2–4.5 °C quoted in many modern day literatures.

Investigations of how CO_2 absorbs radiation were further advanced by S. P. Langley of the Allegheny Observatory in the USA, who designed the device for measuring the solar constant (i.e., the amount of heat radiated by the Sun). Langley was also the pioneer of the link between the variations in atmospheric composition and long-term climate change. In 1940, G.C. Callendar was the first to calculate the warming associated with increase in CO_2 concentration from burning of fossil fuels. He used calculations to link various threads of evidence which had been observed and link them to the theory of global climate change and the role of CO_2 which was widely accepted. Callendar is often regarded as the originator of the modern theory connecting atmospheric CO_2 concentration and global climate change because of his pivotal role in distinguishing the CO_2 absorption bands from that of water vapor which led to current understanding of greenhouse warming. However, his calculations and work did not raise any concern at that time.

The first expression of concerns about climate change which might be brought about by increasing GHGs occurred in 1957 when Roger Revelle and Hans Suess of Scripp Institute of Oceanography in California published a paper which pointed out that the buildup of CO_2 in the atmosphere by human activities is like carrying out a large-scale geophysical experiment. This motivated C.D. Keeling to start the routine measurement of CO_2 concentration at Mauna Loa in Hawaii. Finally, with more accurate measurements of atmospheric CO_2 concentration, Keeling was able to link statistically the evidence for increase in global temperature with increase in atmospheric concentrations of CO_2 (Keeling et al. 1976b). The rapidly increasing use of fossils together with the availability of observatory data confirming the increase of CO_2 and its influence on global temperature lead to the topic of global warming moving up in political agenda. Eventually this political attention led to Climate Change Convention in 1992 and the formation of Intergovernmental Panel on Climate Change (IPCC) under the auspices of the United Nations (UN).

1.3.3 Enhanced Greenhouse Effect

As discussed in the previous section, Earth is a planet in dynamic equilibrium, in that it continuously absorbs and emits electromagnetic radiation. It receives UV and visible radiation from the Sun and it emits IR, and energy balance requires that the energy received must be equal to energy emitted for the temperature of the Earth to be constant. The Earth emits IR radiation with a range of wavelengths spanning from ~4 to 50 μm, and the majority of emission are in the range 5–25 μm (400–

2000 cm^{-1}). The argument that greenhouse effect has maintained Earth at a stable temperature assumes that the concentration of trace gases remains constant over a long period of time. But this is not the case for CO_2, CH_4, N_2O and O_3. Their concentrations in the atmosphere have increased substantially since the industrial revolution, circa 1750 due to the anthropogenic activities (Table 1.1).

In addition, some man-made GHGs that are not naturally occurring which are more potent heat absorbers, including hydrofluorocarbons (HFCs), perfluorocarbons [PFCs; a class of organofluorine compounds that have all hydrogen (H) replaced with fluorine (F)], and sulfur hexafluoride (SF_6) generated from a variety of industrial processes have been added to the atmosphere (Baede et al. 2001). These compounds are the most potent GHGs because they have large heat-trapping capacity and some of them have extremely long atmospheric lifetimes (Table 1.2). Once emitted, these GHGs can remain in the atmosphere for centuries, making their accumulation almost irreversible. The amount of water vapor in the atmosphere mostly depends on the temperature of the surface of the ocean, since oceans cover larger Earth's surface than the lands. Most of it originates from evaporation from the ocean surface, and is not directly influenced by anthropogenic activities. The amount of radiation trapped in the atmosphere depends on gaseous composition of the atmosphere and the spectral properties of the gases.

Table 1.2 Atmospheric lifetimes and the global annual mean surface dry-air mole fraction of greenhouse gases (Hartman et al. 2013; WMO 2016)

Greenhouse gas	Atmospheric lifetime (years)	Recent (2015) tropospheric concentration	Global warming potential (100-yr time horizon)	Industrial Era increased radiative forcing (W m^{-2})
Conentrations in parts per million (ppm)				
Carbon dioxide (CO2)	100–300	400.1 ± 0.1 ppm	1	1.94
Conentrations in parts per billion (ppb)				
Methane (CH4))	9.1	1845 ± 2 ppb	28	0.50
Nitrous oxide (N2O)	131	328 ± 0.1 ppb	265	0.20
Tropospheric ozone (O3)	hours-days	237 ppb	n.a.	0.40
Conentrations in parts per trillion (ppt)				
Sulfur hexafluoride (SF_6)	3200	8.6 ppt	23,500	0.005
CFC-11	45	232	4,660	0.06
CFC-12	100	516	10,200	0.166
CFC-113	85	72	5,820	0.022
HCFC-22	11.9	233	1,760	0.049
HCFC-141	9.2	24	782	0.004
HFC-134a	13.4	84	1,300	0.013

Anthropogenic activities in post-industrial era have resulted in enhanced emission of four major GHGs namely CO_2, CH_4, N_2O, and O_3. It is the changes in the concentrations of these gases that has caused enhanced greenhouse effect to occur in the post- industrial era. The increase in the concentration of GHGs causes imbalance in radiation budget. By trapping more IR radiation, the Earth's surface responds by warming to restore the energy balance. The atmospheric concentration of CO_2 has increased due to fossil fuel use in transportation and power generation, cement manufacturing, deforestation and accelerated processes of organic matter decomposition. The CH_4 has increased because of agricultural activities, natural gas distribution, and landfills. Wetlands also release CH_4 naturally. The N_2O has increased as a result of agricultural soil management and N fertilizer use, livestock waste management, mobile and stationary fossil fuel, combustion, and industrial processes. Soils and oceans also emit N_2O naturally. Hydrofluorocarbons (HFCs) are man-made chemicals developed as alternatives to ozone-depleting substances for industrial and consumer products, for example, HFC-134a, used in automobile air-conditioning and refrigeration. Perfluorocarbons (PFCs) are chemicals primarily produced from aluminum production and semi-conductor manufacture, while sulfur hexafluoride (SF_6) is a gas used for insulation and protection of current interruption in electric power transmission and distribution equipment. Other GHGs include ozone (O_3) continually produced and destroyed in the atmosphere by chemical reaction.

Anthropogenic activities have increased O_3 in the troposphere (i.e., the atmospheric layer closest to the Earth) through the release of gases such as CO, hydrocarbons, and NO which chemically reacts to produce O_3 (Forster et al. 2007; Myhre et al. 2013). Changes in atmospheric water vapor and O_3 are climate feedbacks due to indirect effect of anthropogenic activities. Because GHGs absorb IR radiation, changes in their atmospheric concentration alter the energy balance of the climate system. Increase in atmospheric GHGs concentrations produces net increase in absorption of energy of the Earth, leading to warming of Earth's surface.

The characteristic absorption of CO_2 in the IR radiation range of the atmospheric window of the Earth makes it a potent GHG. Since 1980s, a scientific consensus has emerged that human activities through increasing the concentration of GHGs in the atmosphere have enhanced the greenhouse effect and set in motion a global warming trend (IPCC 2001, 2007, 2013). For example, CO_2 in the atmosphere has increased from about 280 ppm in pre-industrial era (1750) to the current 400.0 ± 0.1 ppmv (WMO 2016). Similarly, concentrations of CH_4 and N_2O have increased from 700 and 270 ppb in pre-industrial era to current levels of 1845 ± 2 and 328 ± 0.1 ppbv, respectively (WMO 2016). This change represents an abundance of 144, 256, and 121 for CO_2, CH_4, and N_2O, respectively, relative to year 1750. The mean growth rate estimates of CO_2 concentration in the atmosphere is at 2 ppm yr^{-1} over the past 10 years (WMO 2016).

The increase in atmospheric CO_2 concentration has contributed about 72% of the enhanced greenhouse effect to date, CH_4 about 21%, and N_2O about 7% (Houghton 2009). The CO_2 is stronger in enhancing greenhouse effect because its strong IR absorption band at 15 μm (Fig. 1.2) occurs close to the peak of blackbody function at the temperatures representative of the Earth's atmosphere and surface (Zhong and

Haigh 2013). Therefore, anthropogenic activities have dramatically altered the chemical composition of the global atmosphere with great implications for current and future climate. Atmospheric theory predicts that changes in the concentration of trace gases will have dramatic consequences for the habitability of the earth, which may include (i) food insecurity, (ii) loss of biodiversity and ecosystems change (iii) destruction of the stratospheric ozone layer due to increase in N_2O and halogenated compounds, and (iv) increase in the amount of tropospheric ozone due to increased emissions of NO_x, CO, and hydrocarbons. With the current trends, the earth is likely to warm by 3–5 °C for the next century (Le Treut et al. 2007). This is as much as it has warmed since the last ice age. Such a warming would have adverse impacts on ecosystems because of inability to adjust to such a rapid temperature changes.

Although the atmospheric concentrations of CH_4 and N_2O are much lower than that of CO_2, they each make a disproportionate contribution to atmospheric anthropogenic greenhouse effect in relation to their concentrations in the atmosphere. Methane contributes some 15%, and N_2O 6% of the greenhouse effect, making them the second and third most important GHGs after CO_2. This is because CH_4 has a global warming potential 28 times and N_2O is 265 times that of CO_2 on 100-year timescale (Hartmann et al. 2013).

1.4 Natural Versus Anthropogenic Climate Change

1.4.1 Climate System

Climate system is a composite system consisting of five main interactive components, namely the: (1) atmosphere, (2) hydrosphere, (3) cryosphere, (4) lithosphere, and (5) biosphere. These are forced by various external forcing mechanisms; the most important one is the Sun (Fig. 1.1). All the systems are open, interactive, and linked by complex feedbacks processes and a great variety of timescales within the individual components. A change in one part of subsystem may eventually affect all other parts. Feedback processes from the slower subsystems such as hydrosphere (i.e., oceans) or cryosphere (i.e., glaciers) can initiate quasi-periodicities with very long time scale in the faster responsive subsystem such as atmosphere. This leads to what is generally known as climatic cycles and climate change. The atmosphere, hydrosphere, cryosphere and biosphere generally act as a cascading system linked by a complex system of fluxes of energy, momentum and matter across the boundaries and generating numerous feedback mechanisms.

The climate system evolves in time under the influence of its own internal dynamics and due to changes in the external factors that affect global behavior known as “forcings”. Two main external forcing that provide external energy input to the climate system are solar radiation and the earth rotation which causes gravitational energy. However, solar radiation is regarded as the primary forcing mechanism since it provides all the energy that drives the climate system. The spherical shape of the Earth, its rotation and orbital characteristics also influence the climate system. Within the climate system, the energy occurs in different forms including heat, potential energy, kinetic energy, chemical energy, short and long wave radiation. Within the climate system, the atmosphere, hydrosphere, cryosphere, lithosphere, and biosphere act as a cascading system interconnected by flows of energy, momentum and matter.

The shortwave solar radiation is unequally distributed over different parts of the climatic system due to spherical nature of the Earth, the orbital motion and the tilt of Earth's axis. As a result, more radiation is absorbed in the inter-tropical regions than at polar latitudes, leading to excess energy in the tropics and deficit in the polar (40°) latitude. This source and sink of energy distribution is the main cause of thermodynamic processes occurring inside the climatic system such as general circulations in atmosphere and oceans. Except for small imbalances, the Earth system loses the same amount of energy through infrared radiation as it gains from the incoming solar radiation (Fig. 1.1). The direct effect of human activities on climate system is also considered an external forcing.

1.4.1.1 Atmosphere

The atmosphere is comparatively a thin film which comprises the mixture of gaseous envelope surrounding the Earth and formed by several layers of different compositions and nature of energy involved. Atmosphere is the most unstable and rapidly changing part of the climatic system. In the vertical direction, more than 99% of its mass is found below the altitude of only 30 km. The atmosphere can be divided into several layers which differ in composition, temperature, stability, and energy (Fig. 1.4). The main layers from Earth's surface are troposphere, stratosphere, mesosphere, and thermosphere; each separated by conceptual partition called pauses (e.g., tropopause). The composition of the atmosphere up to the mesopause is generally uniform in terms of O_2, N_2 and other inert gases. The abundance of molecules per unit volume is greater at sea level due to higher pressure (Fig. 1.4). The troposphere contains about 80% of the atmospheric mass (Warneck 1988). Among the variable components, water vapor is found predominantly in the lower troposphere and ozone in the middle stratosphere. The CO_2, which has been increasing in recent times, is well mixed below the mesopause. The composition of the atmosphere is further complicated by the presence of various substances in suspension, e.g., liquid and solid water (clouds), dust particles, sulfate aerosols, and volcanic ash. The concentrations of these aerosols vary in time and space. The atmosphere composition is relatively well mixed, therefore changes in its composition can be assumed as first index of changes in global biogeochemical processes.

The atmosphere has evolved as a result of the history of life on the Earth, and is now changing rapidly as a result of human activities, as some evidence presented in next chapters will reveal. The atmosphere is the climatic system component most

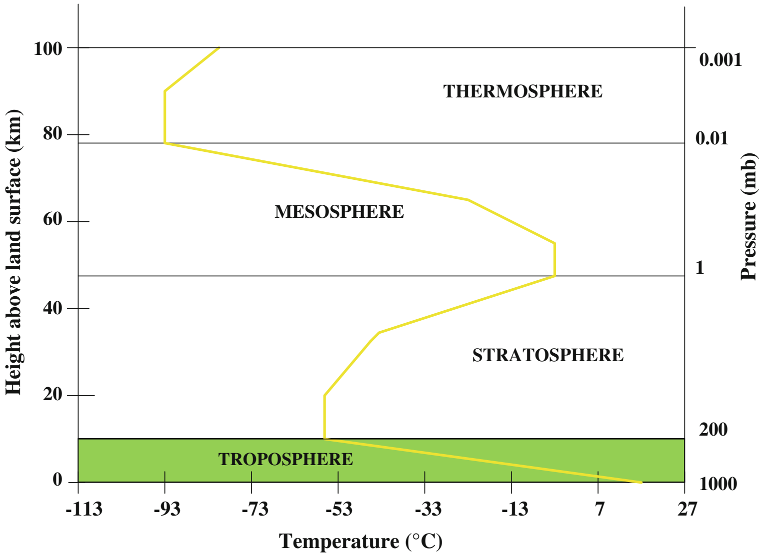

Fig. 1.4 Temperature and pressure profile of the atmosphere to 100 km with estimated subdivisions of the atmosphere. Modified from Peixoto and Oort (1992), Schlesinger (1997)

variable in time and space and exhibit the shorter response time to an imposed change or perturbations applied to its boundary conditions or forcings, mostly due to its compressibility, and low specific heat. These properties make the atmosphere more fluid and unstable. The troposphere shows a large-scale general circulation with eddy motions in the mid-latitudes such as weather systems and random turbulent motions mainly in the planetary boundary layer and near jet streams. These circulations transport biogeochemical constituents between land and sea, causing the circulation of elements (Fig. 1.4).

The atmosphere is held on Earth's surface by the gravitational attraction of the Earth. At any altitude, the downward pull is related to the mass of the atmosphere e.g., (Eq. 1.4):

$$F = Mg \tag{1.4}$$

where, g is the acceleration due to gravity. The pressure decreases with increasing altitude (Fig. 1.5) because the mass of the overlying atmosphere is smaller (Walker 1977). Because of gravity, the atmosphere is stratified with dense layers at the surface, and the atmosphere is in a state of almost hydrostatic equilibrium in the vertical. The atmosphere is set into motion primarily through differentiated heating by the Sun. Motions in the atmosphere are influenced by many other factors including rotation of the Earth. The atmosphere controls Earth's climate and determines the environment in which living creatures live.

1.4.1.2 Hydrosphere

Hydrosphere consists of all water in liquid phase distributed on the Earth. It includes oceans, seas, lakes, rivers, and subterranean waters. The most important for the climatic studies are the oceans which covers approximately two thirds of the earth's surface, so that most of the solar radiation reaching the Earth's surface falls on oceans and is absorbed by the oceans. Because of this large mass and specific heat, the oceans form a large reservoir to store energy. Energy absorbed by the oceans results in relatively small change of surface temperatures compared to that which would have occurred over the land. Due to their thermal inertia, the oceans act as a buffer and regulator for the temperature. Because oceans ore more dense than the atmosphere, they also have a large mechanical inertia and more pronounced stratification. The upper part of ocean is the most active. It contains surface mixed layer with thickness on the order of 100 m. the oceans show much slower circulations than the atmosphere. They form large circulation gyres with the familiar ocean currents and slow thermocline overturning due to density variations associated with changes in temperature and salinity.

The response or relaxation time for the oceans varies within wide range that extends from weeks to months in the upper mixed layer to seasons in the thermocline—at several hundred meters depth to centuries and millennia in the deep ocean. The ocean currents transport part of heat energy stored in the oceans from the inter-tropical regions where there is an excess of heat due to more incident solar radiation towards colder mid-latitudes and Polar Regions. The atmosphere and oceans are strongly coupled. Air—sea interactions occur on many scales in space and time through the exchanges of energy matter and momentum at the atmosphere —ocean interface. The exchange of water vapor through evaporation into the atmosphere supplies the water vapor into the atmosphere and part of energy for the hydrological cycle leading to condensation, precipitation, and runoff. Precipitation strongly influences the distribution of ocean salinity. The lakes and subterranean waters are essential elements of terrestrial part of the hydrological cycle and also play important role in global climate. They also influence the climate on regional and local scale. Rivers are also an important factor in ocean salinity near coasts.

1.4.1.3 Cryosphere

Cryosphere comprise a large masses of snow and ice of the Earth's surface. It includes the extended ice fields of Greenland and Antarctica, another continental glaciers and snow fields, sea ice and permafrost. The cryosphere is the largest reservoir of freshwater on earth. Its importance in climatic system results mainly from its albedo (i.e., high reflectivity of solar radiation) and its low thermal conductivity. Continental snow cover and sea ice change seasonally leading to large intra- and inter annual variations in energy budget of the continental regions and of the upper mixed layer of the ocean. Due to the high reflectivity of snow and ice for solar radiation and low thermal diffusivity of sea ice compared to that of stirred water, the snow and ice act as insulators for the underlying land and waters, preventing it from losing heat to the atmosphere. The strong cooling of the atmosphere near the Earth's surface stabilizes the atmosphere against convection and contributes to the occurrence of colder local climate. The continental ice sheets play a major role in climatic changes on a much longer time scales—up to tens of thousands years such as the glacial and interglacial periods that occurred during Pleistocene.

1.4.1.4 Lithosphere

The lithosphere includes the continents whose topography affects air motion and the ocean floor. Excluding the upper active layer, in which temperature and water content can vary as a response to the atmospheric and oceanic processes, the lithosphere has the longest response time of all climatic system. Lithosphere can almost be considered as a permanent feature of climatic system. There are strong interaction of lithosphere with the atmosphere through the transfer of mass, angular momentum and sensible heat and also the dissipation of kinetic energy by friction in the atmospheric boundary layer. The transfer of mass occurs mainly in the form of water vapor, rain, snow, and in the form of other particles and dust. Volcanoes throw matter and energy from the lithosphere into the atmosphere, and increase the turbidity of the air. The added particles as well as sulfur-bearing gases that may have an important effect in radiation balance of the atmosphere and therefore on the Earth's climate (Mass and Portman 1989). There is also a large-scale transfer of angular momentum between lithosphere and the oceans, presumably through the action of torques between the ocean and continents. The soil moisture of the most active layer of the continental lithosphere influence the local energy balance by affecting the rate of evaporation, the surface albedo and the thermal conductivity of the soil.

1.4.1.5 Biosphere

The biosphere consists of the terrestrial vegetation, continental flora and fauna and oceanic fauna. The vegetation alters the surface roughness, surface albedo, evaporation, runoff, and field capacity of soil. In addition, the biosphere influences CO_2 balance in the atmosphere and oceans through photosynthesis and respiration (Fig. 1.5). The biosphere is sensitive to the changes in the atmospheric climate and it is through the signature of these changes in fossils tree rings pollen etc. during the past ages that the information on the paleo-climates of the Earth was obtained. Human interaction with the climatic system through anthropogenic activities such as agriculture, urbanization, industrialization and pollution are among important variables.

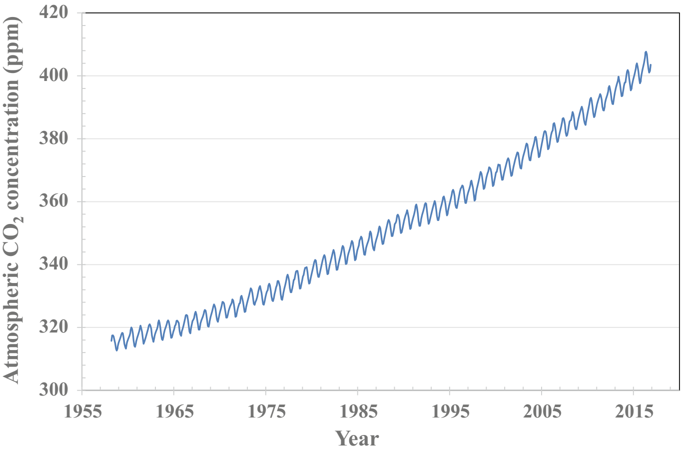

Fig. 1.5 Mean monthly atmospheric CO_2 concentration for Mauna Loa Observatory station from 1958 to November 2016 showing seasonal variability for summer and winter CO_2 emissions patterns. Data from NOAA/ESRL (2016)

1.4.2 Climate Change

Climate change refers to a change in state of climate that can be identified by changes in mean and/or the variability of the properties and that persists for an extended period of time (i.e., change in the state of the climate that can be identified by using statistical tests), typically decade or longer. Climate changes may be due to internal process or external forcings such as modulation of solar cycle, volcanic eruptions and persistent anthropogenic changes in the composition of the atmosphere or land use. The United Nation Framework Convention on Climate Change (UNFCCC) defines the climate change as a change in climate which is attributed directly or indirectly to human activities that alter the composition of the global atmosphere and which in addition to natural climate can be observed over comparable time periods. The UNFCCC therefore, makes distinction between climate change attributable to human activities altering the atmospheric composition and climate variability attributable to natural causes. Human activities such as emission of GHGs or land use change do result in external forcing. The large-scale aspects of human-induced climate change are partly predictable. However, the ability to predict the climate change is limited because of lack of accurate prediction of population change, socio-economic change, technological development, and other characteristics of future human activity.

Climate variability denotes deviations of climate conditions over a period of time due to natural phenomena (WMO 2015). Various examples of these anomalies in climate exists, including Inter-decadal Pacific Oscillation (IPO) which causes decadal changes in climate averages, the El-Nino-La Nina Southern Oscillation (ENSO) resulting from the interaction between atmosphere and ocean in the tropical

Pacific, which causes much variability throughout many tropical and sub-tropical regions, and the North Atlantic Oscillation (NAO) that provides climate perturbations over Europe and Northern Africa (Salinger 2005). In contrast to these natural changes, climate change is generally associated with anthropogenic causes, and it can result into permanent climatic changes.

Global climate is determined by radiation balance of the Earth. Earth's radiation balance can change due to (1) changes in the incoming solar radiation—which may occur due to changes in the orbit of the Earth or the Sun itself, (2) changes in the fraction of solar radiation that is reflected (i.e., change in albedo), and (3) alteration of long wave energy radiated to the space (i.e., change in GHGs concentration). Regular cycles of pre-industrial era climate changes, including several ice ages over the past three million years, have been attributed to regular variations in Earth's orbit around the Sun. These natural changes are sometimes called Milankovitch cycles. These include changes in the amount of solar radiation received at each latitude in each season. Exactly how this starts and ends ice ages is still a topic of discussion among climatologists. Climate model simulations have confirmed that an Ice Age can be started this way. Atmospheric CO_2 concentration also plays important role in ice ages and natural climate change. Ice core data show that CO_2 concentration is low in the cold glacial times (<190 ppm) and high in warmer inter-glacial ($\sim$280 ppm). Changes in ocean circulation and heat transport can also cause abrupt climate changes which do not involve change in global radiation balance. These can be triggered by instabilities in the ice sheets surrounding the Atlantic and the associated fresh water release into the ocean.

Human beings have influenced their environment. However, it is only since the beginning of Industrial Revolution that the impact of human activities began to extend to much larger scale—continental and global, with the potential impact on regional and global climate. Global warming is one aspect of climate change which is actually induced by anthropogenic activities. Although the past changes in global temperatures have been inferred, the current temperature rising can be directly associated with human activities which has increased the concentration of heat trapping GHGs in the atmosphere, and the feedback mechanism for the restoration of the energy balance is the global temperature rise. Anthropogenic activities contribute to climate change by causing changes in Earth's atmospheric composition of GHGs and aerosols. Since industrial revolution, the concentration of GHGs has been increasing. Changes in atmospheric CO_2 concentration in particular and its role in anthropogenic climate change are the focus of this book, and will be discussed in more details in the following chapters. The last part of the book will discuss the mitigation strategies for increase in CO_2 and adaptation for climate change.

The most well-known effects of elevated atmospheric CO_2 concentration and other GHGs is the increased interception of outgoing IR radiation (i.e., radiations from the Earth). The increase in GHGs, thus, changes the radiation balance of the Earth such that previous steady state is disturbed and more radiation now reaches the Earth's surface than is lost from it, consequently causing the global warming. It is estimated that, averaged over the globe, air temperatures at the surface of the Earth rose by 0.75 °C during the 20th century with higher warming over land than over oceans (IPCC 2007; Hansen et al. 2006). In addition, the data suggests that the top 300 m of the ocean warmed by an average of about 0.2 °C between mid-1950s and the turn of 20th century, and about 0.6 °C over the past century. Over the past three decades, changes in atmospheric concentration of GHGs has increased the global temperature at approximately 0.2 °C decade^{-1} (Hansen et al. 2006) with much of the additional energy absorbed by the world's oceans. Warming is much more in western Equatorial Pacific than Eastern Equatorial Pacific over the last century. Water has much more heat inertia than air. The volumetric heat capacity of sea water is about 4 J cm^{-3} K^{-1} compared with about 0.001 J cm^{-3} K^{-1} for the air at the sea level (Tyrrell 2011). Because of large heat capacity, oceans have much longer response time—typically decades up to centuries or millennia. As a result, more than 80% of extra heat retained by the enhanced greenhouse effect has entered the oceans. Because more heat is needed to heat water, inertia of the oceans introduce time lag into the global warming response to elevated GHGs, and the global temperature rise has not yet experienced all of the heating associated with the current radiation imbalance. This implies that even if emission of GHGs to the atmosphere is stabilized, global warming will continue for decades to come due to slow response of the ocean (Wigley 2005).

Climate change is one of the most serious environmental challenges of the 21st century. Emission of CO_2 from anthropogenic activities; mainly fossil fuel combustion, cement production, and changes in land use—mainly deforestation; are the main drivers of the climate change (Ciais et al. 2013). Currently, 90% of the energy carriers used globally is of fossil origin and their use is associated with emission of CO_2 which was not available for global C cycling. Every year, the atmosphere receives over 15 Pg of CO_2, and fossil fuel combustion is the dominant source (Tans 2009). Accurate and systematic measurements of atmospheric CO_2 concentrations at Mauna Loa, Hawaii and South Pole were started by C.D. Keeling in 1959 (Keeling et al. 1976a, b). The 1750 globally averaged abundance of atmospheric CO_2 based on measurements of air extracted from ice core and firn is 278 ± 2 ppm (Etheridge et al. 1996).

Averaged mole fractions since start of the instrumental records for Mauna Loa Observatory are plotted in Fig. 1.5. The important features in the contemporary CO_2 record are the long-term increase and the seasonal cycle resulting from photosynthetic and respiration in the biosphere mostly in the Northern Hemisphere. The main contributors to the increasing atmospheric CO_2 abundance are fossil fuel combustion and land use change. During the last few decades most of the increasing atmospheric burden of CO_2 is from fossil fuel combustion. In 2005, the atmospheric CO_2 concentration was 379 ppmv Table 1.1 (AR4, IPCC 2007) and has increased to 390.5 ppm in 2011 and 400 ppmv in 2015, an average increase of 1.7 ppm yr^{-1}. From 1980 to 2011 the average annual increase is 1.7 ± 0.5 which corresponds to global burden of to 2.1 Pg C yr^{-1}. Since 2001, CO_2 has increased at 2.0 ± 0.3 ppm yr^{-1}. The rate of increase varies from year to year from 1980, the lowest increase was 0.7 ± 0.1 ppm in 1992 and highest at 2.9 ± 0.1 ppm in 1998. Most of the inter-annual variability in growth rate is driven by changes in the balance between photosynthesis and respiration on the land each having global fluxes of 120 Pg C yr^{-1}.

The atmospheric CO_2 concentration was 390.5 ppm in January 2011, and increased to 400 ppm by 2015 (WMO 2016; CDIAC 2015). Emissions from fossil fuel combustions are estimated at 9.2 Pg yr^{-1} (CDIAC 2015). Demand for energy and associated services to meet social and economic development and improvement of welfare of the mankind is growing with increase in the global population. CO_2 emissions resulting from energy generation are the main drivers of historic and future atmospheric CO_2 increase. Biofuels are currently the only significant sustainable source that can partially replace fossil fuels in the short term (Sun and Cheng 2002; Hamelinck et al. 2005), while the technology to transform the economic and transportation sectors to move away from fossil fuel combustion develops. It is pertinent to understand the detailed C cycling with emphasis on the role of fossil fuels in transforming geologically stored C into actively cycling of C.

1.5 Conclusions

The climate system energy is explained with the revised budget necessitated by recent and more accurate measurements at the top of atmosphere obtained recently from instruments mounted on satellites orbiting the Earth. In addition, more and more of the Earth's surface infrared heat measurement are now available, which reduces the uncertainty in global radiation budgets and increases the understanding of the role of enrichment in the concentration of GHGs in the observed global temperature rise. Anthropogenic activities of fossil fuel burning and land use emissions have dramatically altered the atmospheric composition of GHGs with the attendant effects of increasing the global temperature by 0.8 °C since the Industrial Revolution. The decade between 2000 and 2011 is the warmest in the past thousand years. Atmospheric concentration of CO_2 is increasing at 2 ppmv yr^{-1} in the last 5 years, which is equivalent to global atmospheric burden of 2.1 Pg yr^{-1}. Carbon dioxide currently contributes 72% of the anthropogenic greenhouse effect due to its stronger absorption band for infrared heat which coincides with strongest blackbody radiation band of the Earth surface.

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Chapter 2
Variability and Change in Climate

Abstract Understanding of the current and future climate change requires understanding of mechanisms which controlled climate change both before and after the last glacier ages. Although the Sun played an important role in climate variability and climate change in paleoclimate, it is generally accepted that the Sun has not been a major driver of climate change since the Industrial Era. This chapter describes the observed climate change with particular emphasis on the Industrial Era period. The globally averaged atmospheric mole fraction of carbon dioxide (CO_2) reached the abundance of 144% relative to the preindustrial concentrations in 2015, with many other climate variables setting new records in the past few years. For example, atmospheric abundance of methane (CH_4) and nitrous oxide (N_2O) reached 1845 ± 2 and 328 ± 0.1 ppb in 2015, respectively. Also, 5 major and 15 minor greenhouse gases (GHGs) contributed 2.94 W m^{-2} of the direct radiative forcing which is 36% greater than their contribution at the onset of Industrial Revolution in 1750. The record high radiative forcing has resulted in the highest annual global surface temperature over ~135 years of modern record keeping. Since oceans absorb about a quarter of anthropogenic CO_2 emissions, increase in CO_2 concentration during the Industrial Era has resulted in ocean acidification equivalent to approximately 30% increase in H^+ concentration in ocean water. Other associated changes include increase in sea surface temperature (SST) and increased thermal energy content of the ocean which absorbs 90% of Earths' excess heat from GHG forcing. Also ocean warming and increased stratification of the upper ocean caused by global climate change results in deoxygenation of interior oceans with implications for ocean productivity, nutrient cycling, C cycling and marine habitat. Owing to ocean warming and ice melting, the global sea level rise reached 67 mm greater than the 1993 annual mean, when satellite altimetry measurement began, with salty regions of ocean getting saltier while fresh water regions of ocean parts are getting fresher. CO_2 therefore, remains the single most important anthropogenic GHG, contributing 65% to long-lived GHGs radiative forcing, and responsible for nearly 83% of the increase in radiative forcing over the decade ending in 2015.

Keywords Climate • Global warming • Greenhouse gases • Solar radiation • Solar activity • Ecosystems

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Contents

2.1 Introduction

The Earth's climate system is powered by solar electromagnetic radiation, and any variability of the Sun's radiative output has the potential of affecting climate and, hence the habitability of the Earth (Solanki et al. 2013). However, changes in solar power output on decadal, centennial, and millennial timescales are limited to small changes in the effective global surface temperature on shorter timescales (Lockwood 2012). Sun is the source of practically all external energy input into the climate system. Change in solar radiation can influence climate system through: (a) variations in insolation caused by changes in the Sun's radiative output (i.e., direct influence), (b) modulations of radiation reaching different hemispheres of the Earth through changes in Earth's orbital parameters and in the obliquity of its rotation axis (i.e., indirect influence through changes in Earth's orbit), (c) alterations in the influence of Sun's activity on Galactic cosmic rays which affect the cloud cover (e.g., Marsh and Svensmark 2000), (d) alterations of the fraction of solar radiation that is reflected (a fraction called albedo—it can be changed, for example, by changes in cloud cover, aerosols, or land cover), and (e) variations in the long wave energy radiated back to space (e.g., through changes in atmospheric GHG concentration). In addition, local climate also depends on distribution of heat by winds and ocean currents. All these factors have played some role in the past climate change.

The first of these is generally considered to be the main cause of the solar contribution to the global climate change. Solar variability takes place at many time scales that include 27-day variation due to solar rotation, annual variation due to ellipticity of Earth's orbit, decadal scale solar magnetic cycle (sunspot), and also the oscillation between grand solar maxima and minima on timescales of several centuries (Helama et al. 2010; Lockwood 2012). Variability associated with the 11-year solar cycle has shown to produce measurable short-term climate anomaly (Gray et al. 2010; Lockwood 2012). There is a growing evidence suggesting that changes in solar irradiance affect Earth's middle (between 10 and 50 km) and lower atmosphere (Gray et al. 2010). The second is believed to be the prime cause of the patterns of glacial-interglacial cycles of Ice Age that have dominated the longer term evolution of the climate over the past few million years (refer Chap. 5). The various parameters of Earth's orbital and rotational motion vary at periods of 23,000 years (precession), 41,000 years (obliquity), and 100,000 years (eccentricity) (Crucifix et al. 2006). The third path builds on the modulation of the Galactic cosmic rays by solar magnetic activity. The Sun's open magnetic flux and the solar wind impede the propagation of the charged Galactic cosmic rays into the inner Solar System, so that at times of high solar activity, fewer cosmic rays reach the Earth. Their connection with climate has been drawn from the correlation between the cosmic rays flux and global cloud cover (Marsh and Svensmark 2000). Most of solar irradiance variations are produced by dark (sunspots) and bright (magnetic elements forming faculae) surface magnetic structures on the solar surface, whose concentration changes over the solar cycle. Variations in solar irradiance produce natural forcing of Earth's climate with global and regional scale responses (Lean and Rind 2008). Globally the mean surface temperature varies in phase with solar activity. A number of attempts at reconstructing past climate variations through solar forcing have indicated that before 1940, direct forcing by changes in solar irradiance can explain the large proportion of observed changes. However, it is virtually impossible to assign the global warming of the past half century, and particularly the observed warming since 1975 to variations in solar irradiance alone using either statistical or physical methods. The indirect solar forcing seems to be small and unable to explain the observed warming (Keller 2009).

Earth's climate is the result of balance between incident shortwave solar radiation absorbed and long wave infrared radiation emitted (described in Chap. 1). As the Earth's temperature has remained relatively constant over many centuries, the incoming solar energy must have remained nearly in balance with outgoing radiation. A net change in imposed perturbation of this radiation balance to Earth system, either through anthropogenic activity or natural process is referred to as a *radiative forcing*. The radiative forcing averaged over a particular length of time quantifies the energy imbalance that occurs when the imposed change takes place. Changes in the atmosphere, land, ocean, biosphere, and cryosphere; either natural or anthropogenic can perturb the Earth's radiation budget and produce radiative forcing that could affect the climate.

Changes in global energy budget occur either from changes in net incoming solar radiation or changes in outgoing long wave radiation. Changes in net incoming solar radiation derive from changes in the net Sun's output of energy. A precise record of measurements of total solar irradiance (i.e., the total power of Sun affecting a unit area perpendicular to the Sun's rays in W m^{-2}) extending back to 1978 established a generally accepted value of about 1360.8 ± 0.5 W m^{-2} (Kopp and Lean 2011; Kopp et al. 2012; Solanki et al. 2013), which is responsible for keeping Earth from cooling off to temperatures that are too low for sustaining human life. The composition, structure, and dynamics of Earth's atmosphere also play a fundamental role of making efficient use of the energy input from the sun through the greenhouse effect. The net imbalance between absorbed shortwave radiation and outgoing long wave radiation at the top of the Earth's atmosphere is a fundamental climate variable which represent a nexus between changes in radiative forcing that sets the trajectory of climate change and climate response. The magnitude of climate response is determined by feedbacks which may amplify or diminish climate responses, but also influenced by unforced variability internal to climate system (Hansen et al. 2011). Surface energy fluxes drive ocean circulation, determine how much water is evaporated from the Earth's surface, and govern the planetary hydrological cycle.

Changes in outgoing long wave radiation can result from changes in temperature of Earth's surface or atmosphere or changes in emissivity (i.e., measure of emission efficiency) of long wave radiation or from atmosphere or Earth's surface. Ocean heat content and satellite measurements indicate a small positive energy imbalance (Trenberth et al. 2009, 2015; Murphy et al. 2009; Stephens and L'Ecuyer 2015) that is consistent with rapid changes in atmospheric composition. Over the 1985–1999 period, the imbalance between absorbed shortwave radiation and outgoing long wave radiation at the top of atmosphere was 0.34 ± 0.67 W m^{-2}, and increased to 0.62 ± 0.43 W m^{-2} for 2000–2012 period, despite slower rate of surface temperature increase since 2000 compared with late 20th century (Allan et al. 2014). The changing atmospheric composition, especially due to increase in atmospheric GHGs from human activities, including burning of fossil fuels is responsible for the observed imbalance. Increasing GHGs in the atmosphere causes imbalance to inflow and outflow of energy to the Earth system at the top of the atmosphere by increasingly trapping more radiation, and therefore, creating warming (Trenberth 2009), which can be manifested in many ways, including rising surface temperature, melting Arctic sea ice, increasing the water cycle, and altering storms. Most of excess energy goes into the ocean, however (Trenberth 2009; Bindoff and Willebrand 2007). Over the past 50 years, the oceans have observed about 90% of total heat added to the climate system and the rest about 10% is used to melt sea and land ice, warming the land surface, and warming and moistening the atmosphere (Trenberth 2009). Strengthened ocean heat uptake, especially below 700 m depth after 2000 is responsible for slowing global mean surface air temperature increase during the first decade of 21st century (Watanabe et al. 2013; Balmaseda et al. 2013).

Climate change is driven by disturbances to the energy balance of the Earth system, which are generally termed climate forcings. Climate system also exhibits unforced (i.e., chaotic) variability. However, it is now widely agreed that the strong global warming trend since the late 19th century is caused predominantly by man-made changes in atmospheric composition (Hegerl and Zwiers 2007; IPCC 2014). Increase in atmospheric GHGs concentration (e.g., CO_2, CH_4, and N_2O) makes the atmosphere more opaque at the infrared wavelengths, and this increased opacity reduces transmission of heat to space. The temporary imbalance between the energy absorbed from the sun and heat transmission to space causes the planet to warm until the planetary energy equilibrium is restored. The planetary energy imbalance caused by a change of atmospheric composition defines a climate forcing. The eventual global temperature change per unit forcing (i.e., climate sensitivity) is known with reliable accuracy from Earth's paleoclimate history (Hansen et al. 2011). However, presence of aerosols such as dust, sulfates, and black soot (Ramanathan et al. 2001) in the atmosphere which can both reflect solar radiation to space (cooling effect) and absorb solar radiation (warming effect), and also the efficiency of heat mixing into the deeper ocean limit the ability to predict the global temperature on decadal timescales (Hansen et al. 2011). Ocean heat mixing is a complex and more difficult to simulate by climate models.

Changes in atmosphere, land, and cryosphere can perturb the Earth radiation budget and produce radiative forcing that affect climate. Climate feedbacks, the physical processes that comes into play as climate changes in response to forcing can either amplify or diminish the effects of change in climate forcing. Positive feedbacks amplify while negative feedbacks diminish the climate response. Climate feedbacks do not come into play coincident with the forcing, but rather in response to climate change. Feedbacks operate by altering the amount of solar energy absorbed by the planet or the amount of heat radiated into space, and they tend to be a function of global temperature change. Climate feedbacks can be grouped into fast and slow feedbacks. Fast feedbacks appear almost immediately in response to global temperature change. These include water vapor when its atmospheric concentration is enhanced by increase in surface temperatures (Hansen et al. 2011). Water vapor is a powerful GHG, and its increasing atmospheric concentration enhances the greenhouse effect and leads to further warming (Cubasch et al. 2013). Other fast feedbacks include clouds, natural aerosols, snow cover, and sea ice. Slow feedbacks may lag global temperature change by decades, centuries, millennia or longer timescales (Hansen et al. 2011). The principal slow feedbacks are changes in continental ice sheet area which affect surface reflectivity or albedo, and long-lived GHGs. The objectives of this chapter are to summarize the current knowledge on climate change and roles of both natural processes and anthropogenic activity to set the stage for discussion on the role of C cycling and climate change in the next sections.

2.2 Radiative Forcing

For convenience, factors responsible for climate change are generally separated into forcings and feedbacks. Forcings are energy imbalances imposed on the climate system externally by both natural processes or as a result of human activities (Fig. 2.1). Increase in atmospheric GHGs concentration, particularly CO_2 and CH_4 are the main anthropogenic forcing. Increase in atmospheric GHGs concentration causes warming through their greenhouse effect. As a result of warming, the surface restores the radiative balance by increasing radiation to space, but also warming causes atmospheric water vapor, albedo, clouds, vegetation, ice sheets, permafrost,

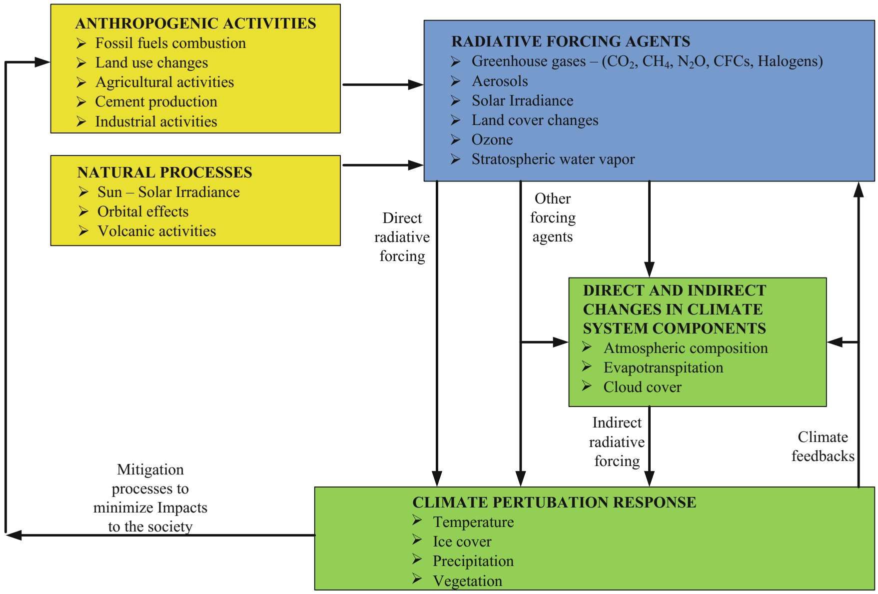

Fig. 2.1 Anthropogenic activities and natural processes effects on climate forcing and associated climate response and feedbacks

and atmospheric chemistry to change. These changes affect the Earth's radiation budget directly or indirectly (Fig. 2.1). Feedbacks are the internal processes that amplifies or dampens the climate response. For example, warmer global temperatures increase atmospheric water vapor, which amplifies the initial warming due to increased atmospheric concentration of GHGs through greenhouse properties of atmospheric water vapor. Also, warmer temperatures lead to melting of snow and ice, which exposes darker surface that absorbs rather than reflecting incoming solar radiation, leading to more warming and melting than it would have occurred if the snow cover had been fixed. Feedbacks can occur at a broad range of timescale, from instantaneous up to thousands of years (Wolff et al. 2015).

The Intergovernmental Panel on Climate Change (IPCC) uses radiative forcing (RF) to assess and compare externally imposed perturbation in radiative energy budget on Earth's climate. Such perturbations can be a result of natural or anthropogenic causes or both. The RF is defined as change in net downward minus upward radiative energy flux at the top of atmosphere (tropopause) due to change in external driver of climate change (Myhre et al. 2013). The RF quantifies the perturbation in radiative fluxes caused by changes in forcing agents such as atmospheric GHGs and expressed in W m^{-2} averaged over a particular period of time. It therefore, quantifies energy imbalance in terms of temperature change that occurs when imposed change takes place. It is computed with all tropospheric properties held at their unperturbed values and allowing perturbed stratospheric temperature to readjust to radiative energy dynamic equilibrium. The IPCC analyses uses 1750 (the beginning of Industrial Era) as a benchmark for assessing changes in climate system caused by human activities and expressed as the changes due to anthropogenic activity. From the beginning of the Industrial Era, the Earth has undergone a very fast and unusual change in RF resulting from anthropogenic actions, which includes increase in atmospheric GHGs concentration, changes in concentration of aerosol particles in the atmosphere and ozone destroying chemicals in the stratosphere as well as changes in the nature of land surface (Table 2.1). The current trajectory of these changes suggests a substantial changes in climate by the end of the 21st century (IPCC 2013).

The utility of the RF concept is that it enables the quantification of various factors that shift the energy balance and assess their relative importance to climate change. The RF can be related through a linear relationship to the global mean equilibrium temperature change at the surface [Eq. 2.1]:

$$\Delta T = \lambda RF \tag{2.1}$$

where, λ is the climate sensitivity parameter (Ramaswamy et al. 2001). The λ derived with respect to RF can vary substantially across different forcing agents (Table 2.1). The forcing factors are external to climate system, and not part of it. The important forcing factors and their estimated values in 2014 are presented in Table 2.1. Equation 2.1 suggests a straightforward calculation of the equilibrium change in temperature at a global scale arising from a particular change in RF if the Earth behaved as simple black body with no additional effects (Knutti and Hegerl 2008). For example, doubling of atmospheric CO_2 concentration results in long-wave forcing of ~ 3.7 W m^{-2}, which would cause an equilibrium warming of ~ 1.2 °C (Knutti and Hegerl 2008). However, in practice the initial perturbation causes a range of other feedback effects (Fig. 2.1), which may weaken (negative feedbacks) or strengthen (positive feedbacks) the global temperature response, and it is the net effect of such feedbacks that determines the sensitivity of climate to forcing. The negative feedbacks (e.g., changes in vertical temperature gradient of the atmosphere) causes the climate to be less sensitive to changes in forcing, while positive feedbacks (i.e., albedo feedbacks) causes the climate to be more sensitive. The nature and magnitude of these feedbacks are the principal cause of the uncertainty in response of global climate to different emission scenario and GHGs concentration pathway over multi-decadal and longer periods (Wolff et al. 2015). Feedbacks also play role in inducing regionally variable responses to climate forcing, both in temperature and other variables such as rainfall and occurrence of extreme events. The RF and their responses are assumed to be additive, making it a useful tool for designing policies towards a climate change mitigation target. Analysis of forcing due to observed or modeled concentration changes between pre-industrial and a selected later year provides indication of relative importance of different forcing agents during the period (Table 2.1). The combined effects of all feedbacks are significantly positive (IPCC 2013).

Application of RF concept in climate change detection and prediction has some limitations, including its inability to include other associated climate change

Table 2.1 Global average anthropogenic and natural radiative forcing estimates for the period 1750 to 2014

Parameter	Concentration in 2015*	Lifetime (years)	Average RF 1750 to 2015 (W m^{-2})	Range (W m^{-2})	Source
Carbon dioxide (CO_2)	401.6 ± 0.1		1.91	1.71–2.10	Butler and Montzka (2015) Myhre et al. (2013)
Methane (CH_4)	1833 ± 1	9.1	0.50	0.45–0.55	
Nitrous oxide (N_2O)	327 ± 0.1	131	0.19	0.16–0.22	
Well-mixed GHGs			2.60	2.32–2.87	
CFC-11	233.5 ± 0.8	45	0.058		Butler and Montzka (2015) NOAA/ESRL (2016) Myhre et al. (2013)
CFC-12	578.5 ± 1	100	0.166		
CFC-113	72.2	85	0.116		
HFC-125	15.95	28.2			
HFC-134a	60.7	13.2			
HFC-143a	15.31	47.1			
HFC-152a	6.63	1.5			
HFC-23	9.03	222			
HCFC-22	231.1	11.9			
HCFC-141b	24.1	9.2			
HCFC-142b	219	17.2			
CCl_4	83.4	26			
CH_3Cl_3	3.4	5			
SF_6	8.76	3200			
CF_4		50,000			
C_2F_6		10,000			
Total halogens	–	–	0.36	0.32–0.40	
Tropospheric ozone	–	–	0.40	0.20–0.60	Myhre et al. (2013)
Stratospheric ozone		–	−0.05	−0.15 to +0.05	
Stratospheric water vapor			0.07	0.02–0.12	
Aerosols			-0.80	−1.2 to +0.15	
Surface albedo			0.04	0.02–0.09	
Contrails			0.06	0.005–0.15	
Solar irradiance			0.05	0.0 to +0.10	
Total RF	–	–	2.94 ± 0.03		

*CO_2 concentration in parts per million (ppm), CH_4, N_2O concentration in parts per billion (ppb), All halogens concentration in parts per trillion (ppt)

impacts such as changes in precipitation, surface sunlight available for photosynthesis, extreme events, and regional temperatures which can differ greatly from the global mean temperature. Although it is useful in understanding global mean temperature change, it provides only limited perspective on factors driving broader climate change. In addition, the RF matric does not allow comparison on effects such as the influence of land cover change on evapotranspiration (Andrews et al. 2012). Despite these limitations, the observed changes in climatic variables approximately scale with temperature (Tebaldi and Arblaster 2014; Herger et al. 2015), suggesting that the global temperature is probably the best proxy for the aggregated impacts of forcings and feedbacks, even though the relation is likely nonlinear. Global temperature is relatively easier to measure, and its record extends further back than measurements of most other climate variables. In addition, global temperature can be reconstructed from paleodata, which is not the case for other climate quantities.

2.3 Detection and Attribution of Climate Change

In the IPCC assessments, detection and attribution of climate change involves quantifying the evidence linking external drivers of climate change and observed change in climatic variables. Detection and attribution, therefore, attempts to separate the observed climate changes into components that can be explained by variability generated internally within the climate system and components that are the result of forcings external to the climate system. Atmospheric processes that generate internal climate variability are known to operate on time scales ranging from instantaneous to years. Examples of internal climate variability include water vapor condensation in clouds, inter-hemispheric exchange, and troposphere-stratosphere exchange which operate on short timescales. In addition, internal variability can also be produced by interaction between components, such as El Niño Southern Oscillation (ENSO) produced by coupled ocean-atmosphere phenomenon oscillation occurring in the tropical Pacific (Toniazzo 2006; Toniazzo and Scaife 2006; Hertig et al. 2015). Other components of climate system such as the ocean and large ice sheets operate at a longer timescales. Greenland and Arctic ice sheets are important cryosphere elements affecting both regional and global climate by causing polar amplification of surface temperatures, a source of fresh water to the ocean, and also representing a potentially irreversible change to the state of Earth system as they disappear (Jacob et al. 2012; Seo et al. 2015).

The initial goal of the detection and attribution was to determine whether RF due to GHGs increase has influenced the climate by quantifying uncertainty through simulations of temperature changes with observations (Allen et al. 2000; Houghton et al. 1996; Gillett et al. 2002; Stott and Kettleborough 2002). Subsequently, detection and attribution methods are also used to evaluate the ability of climate models to simulate the observed climate change, assess the role of external factors versus climate variability in observed climate change, and enable the prediction of future climate change based on the changes that have been observed so far (Hegerl and Zwiers 2011; Bindoff et al. 2013; Stott et al. 2016).

Detection of change is a process of demonstrating that climate and/or the system affected by the climate has indeed changed in some defined statistical sense without providing reasons for the detected change (Hegerl et al. 2010). The identifiable change is detected in observations if the likelihood of occurrence of change by chance due to internal climate variability is small. Attribution is a process of evaluating the relative contributions of multiple causal factors responsible for the detected change or event, with an assignment of statistical confidence. Attribution requires the detection of a change in the observed variable or closely associated variables (Hegerl et al. 2010; Bindoff et al. 2013). Therefore, detection and attribution seeks to determine whether climate is changing significantly and if so, what has caused such changes. Such an understanding has several applications: (i) to know if GHGs emission are contributing significantly to climate change, and therefore need to reduce emissions if they are, (ii) to understand the current risks of extreme weather events. Under a non-stationary climate, the traditional definition of climate as statistics of the weather over a fixed 30-year period can no longer hold, since the definition assumes that the climate is stable, as had been traditionally, and what were previously rare events could be already much more common, consequently, general circulation models are needed to characterize the current climate, which can be different from that of previous or succeeding years, and (iii) by comparing observations with models prediction in a rigorous and quantitative way, attribution can improve confidence in model predictions and point out areas where models are deficient and needing improvements.

Although the observational record show clear signs of warming climate, the record does not clearly indicate the causes of the observed changes. Attribution of climate change, i.e., the process of establishing the most likely causes for the detected change with some level of confidence—seek to determine which external factors have significantly affected the climate. External forcing factors are the agents outside the climate system that cause the climate to change by altering the radiative balance or other properties of climate system. Examples of anthropogenic external forcing factors include increase in well-mixed GHGs and changes in sulfate aerosols which affect clouds and make them more reflective and scatter more incoming solar radiation to space, while the external natural forcing factors include solar radiation variability and volcanic activity. Due to internal variability, the attribution statements can never be made with 100% confidence.

The global mean temperature change that results in response to sustained perturbation on the Earth's energy balance after the allowing of enough time for the atmosphere and the oceans to achieve thermal equilibrium is termed as Earth's climate sensitivity. Climate sensitivity has the units of temperature change in W m^{-2}. The sensitivity of climate system to external forcing is governed by the energy imbalances they induce and partitioning of these imbalances between atmosphere, ocean and cryosphere (Trenberth et al. 2009, 2014). However, most of excess energy goes into the global oceans, and oceans act as a large heat sink (Church et al. 2011; Knutti and Rogelj 2015). Equilibrium climate sensitivity combines changes resulting from RF and feedbacks to characterize the temperature response of the Earth to change in forcing (Knutti and Rugenstein 2015). It is defined as the equilibrium global average surface warming in response to RF from an atmospheric CO_2 doubling. It includes feedbacks such as the changes in water vapor, lapse rate, surface albedo and clouds (Knutti and Rugenstein 2015). It is a convenient tool in modeling and policy making for emission control. The incoming solar radiation can also be affected by natural forcing factors including changes in output from the Sun and changes in stratospheric aerosols resulting from volcanic eruptions. The effect of solar forcing on global mean surface temperature trends is considered small, however, with less than 0.1 °C warming attributable to combined solar and volcanic forcing over the period 1951–2010 (Jones et al. 2012a). Variabilities associated with 11-year solar cycle produce measurable short-term regional and seasonal climate anomalies (Lockwood 2012; Gao et al. 2015).

2.4 Climate Change

The Earth's climate history in the past one million years has varied from cold '*icehouse*' conditions, with a documented cold climate and a sequence of glacial-interglacial cycles (Augustin et al. 2004), to a '*warmhouse*' conditions when glaciers generally disappeared in the Northern Hemisphere. The onset of melting of the last glacial maximum ice sheets occurred at approximately 20,000 years ago, a period generally termed as '*last glacial termination*'. It was followed by warmer '*Holocene*', the current interglacial period, where the climate has remained warmer and remarkably stable compared to glacial-interglacial period and favorable for human civilization to flourish. During this stable climate, there have been notable regional climatic fluctuations, of which, the most notable include the period known as '*Little Ice Age*' from 1600 to 1800 when Europe experienced unusually cold conditions and expanded state of glaciers globally (Mann 2002; Matthews and Briffa 2005). Since industrial revolution in 1750, however, increasing evidence points to large human impacts on the planet and global climate to the extent that some scientists and scholars have termed this period as '*Anthropocene*' suggesting that human beings have overwhelmed the forces of nature and become the dominant drivers of global change (Steffen et al. 2007; Waters et al. 2016).

The IPCC (2013) defines climate change as a change in the state of the climate that can be identified using statistical test by changes in mean and/or variability of its properties, and persists for an extended period, typically decades or longer. These changes can be due to either natural processes and/or external forcings. Some external influences such as changes in solar radiation or volcanic activities occur naturally, and can perturb radiation budget while causing variability of the climate system. However, its estimated contribution to currently observed climate change is small (Bindoff et al. 2013). Volcanic eruptions inject aerosols to altitudes as high as 10–30 km in the stratosphere, where they reside for 1–2 years, reflecting sunlight and cooling Earth's surface (Hansen et al. 2011).

The drivers of changes in climate, therefore, include: (i) solar irradiance, (ii) aerosols, (iii) clouds, (iv) ozone, (v) surface albedo changes, and (vi) changes in atmospheric GHGs concentration. The principal global anthropogenic forcing are GHGs and the tropospheric aerosols, mostly in the lower few kilometers of the atmosphere (Myhre et al. 2013). Well-mixed GHGs (e.g., CO_2, CH_4, and N_2O) are closely linked to anthropogenic activities and they also interact strongly with the biosphere and the oceans. Their earlier atmospheric histories have been reconstructed from measurements of air stored in archives trapped in polar ice cores or in firn, and established the pre-industrial (1750) mole fraction of 278 ± 2 ppm, 722 ± 25 ppb, and 270 ± 7 ppb for CO_2, CH_4 and N_2O, respectively (Etheridge et al. 1996, 1998; Prather et al. 2012). Anthropogenic activity increases the atmospheric concentrations of well mixed GHGs, aerosols, and cloudiness. The principal GHGs emitted from anthropogenic activity during industrial era are CO_2, CH_4, N_2O and halocarbons. Systematic measurements of well-mixed GHGs at ambient air concentrations began at different times within the last six decades and expanded to a global monitoring network. The measurements of atmospheric CO_2 started at Mauna Loa, Hawaii, USA in 1958 and established atmospheric mole fraction of 315 ppm in 1958 (Keeling et al. 1976). Direct atmospheric CH_4 measurements of sufficient spatial coverage to calculate the global annual means began in 1978 (Dlugokencky et al. 1994), while that of atmospheric N_2O started in late 1970s.

The global mean abundance of three major anthropogenic GHGs in 2015 were 400.0 ± 0.1 ppm, 1845 ± 2 ppb, and 328.0 ± 0.1 ppb for CO_2, CH_4 and N_2O, respectively (WMO 2016). These values constitute 144, 256 and 121% abundances relative to pre-industrial (i.e., year 1750), respectively, and mean absolute increase of 2.30 ppm yr^{-1}, 11.0 ppb yr^{-1}, and 1.0 ppb yr^{-1} for CO_2, CH_4, and N_2O, respectively during the last 10 years (WMO 2016). The main contributors to the increase in atmospheric CO_2 are fossil fuel combustion and land use change. The average annual increase in globally averaged CO_2 during the instrumental record ranges from 0.49 ppm yr^{-1} to 3.01 ppm yr^{-1} (Fig. 2.2a). About 40% of CH_4 is emitted to the atmosphere by natural sources including wetlands, clathrates, wild ruminants, and termites, and 60% comes from anthropogenic sources such as domesticated ruminants, rice agriculture, fossil fuel exploitation, landfills and biomass burning. The average annual atmospheric CH_4 growth rate decreased from 14.3 ppb yr^{-1} in 1991 to near zero from 1999 to 2006. However, since 2007 atmospheric CH_4 has been increasing again (Fig. 2.2b), and its global annual mean increased by 11 ppb yr^{-1} between 2012 and 2015 (WMO 2016). The N_2O is emitted from both natural (60%) and anthropogenic (40%) sources, which includes oceans, soils, biomass burning, fertilizer use in agriculture, and some industrial processes. Its increase in annual mean for the past 10 years is 1.0 ppb yr^{-1} (Fig. 2.2c). Other anthropogenic GHGs include chlorofluorocarbons (CFCs) and halogenated gases which are also ozone depleting compounds, sulfur hexafluoride (SF_6) produced by chemical industry—mainly as an electrical insulator in power distribution equipment, hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) produced by human activities from various industrial sources. Their current atmospheric concentrations are presented in Table 2.1. While CFCs and most halons are decreasing as a result of regulation of their use under Montreal Protocol, HCFCs and HFCs are increasing at a rapid rates, although they are still low in abundance (WMO 2016; NOAA/ESRL 2016).

Anthropogenic land cover and land use changes are important at local and regional level, but their influence at global level has become less important over the past century (Hansen et al. 2007). Anthropogenic land cover change exerts direct impact on Earth radiation budget through change in surface albedo, modification of surface roughness, and latent heat flux. Land use change, particularly deforestation also has significant effect on well-mixed GHGs emission. Changes in solar irradiance is a natural phenomenon caused by dark regions on the solar disk (Sunspots) which causes slight variations in radiation from the Sun at about 11-year cycles (Seinfeld 2011). The direct radiative forcing as a result of increase in total solar irradiance since 1750 is estimated to contribute an RF ranging from 0.0 to +0.10 W m^{-2} (Myhre et al. 2013; Table 2.1) and the amplification of changes in total solar irradiance by climate system is estimated to cause 20-year lag in climate response (Eichler et al. 2009).

Atmospheric aerosols, both natural and anthropogenic, generally originate from emissions of particulate matter or formation of secondary particulate matter from atmospheric gaseous precursors. The main constituents of the atmospheric aerosols are $SO_4{}^{-2}$, $NO_3{}^{-}$, $NH_4{}^{+}$, sea salt, black carbon (BC), dust, and primary biological aerosol particles (Boucher et al. 2013). Some aerosols increase atmospheric reflectivity of incoming solar radiation and others, such as BC are strong absorbers of energy and also modify shortwave radiation (Heald et al. 2014). Aerosols can also influence clouds albedo by serving as cloud condensation nuclei or ice nuclei. Atmospheric aerosols are some of the most uncertain driver of global climate change, because they can scatter or absorb radiation, thereby cooling or warming the Earth and the atmosphere directly (Heald et al. 2014). The overall impact of present-day atmospheric aerosols is estimated to be cooling, thereby counterbalancing some of warming associated with GHGs (Table 2.1; Myhre et al. 2013).

Cloud may be composed of liquid water (possibly in a super-cooled form), ice, or both (i.e., mixed phase). Clouds cover about two thirds of the globe (Stubenrauch et al. 2013; Stengel et al. 2015). Satellite data estimates that global annual shortwave cloud radiative effect of approximately −50 W m^{-2} and greenhouse effect contribution of +30 W m^{-2} through long wave radiative effect (Loeb et al. 2009; Stephens and L'Ecuyer 2015), implying a net cooling effects of clouds. The net downward flux of radiation at the surface is sensitive to vertical and horizontal distribution of clouds, however. In addition to increasing albedo and causing cooling of the planet, clouds can also exert radiative effect at the surface and within the troposphere, thus influencing the hydrological cycle and circulation. Overall, the net effect of clouds to climate depends on its physical properties—such as level of occurrence, vertical extent, water path, nature of cloud condensation nuclei population, and effective cloud particle size (Boucher et al. 2013).

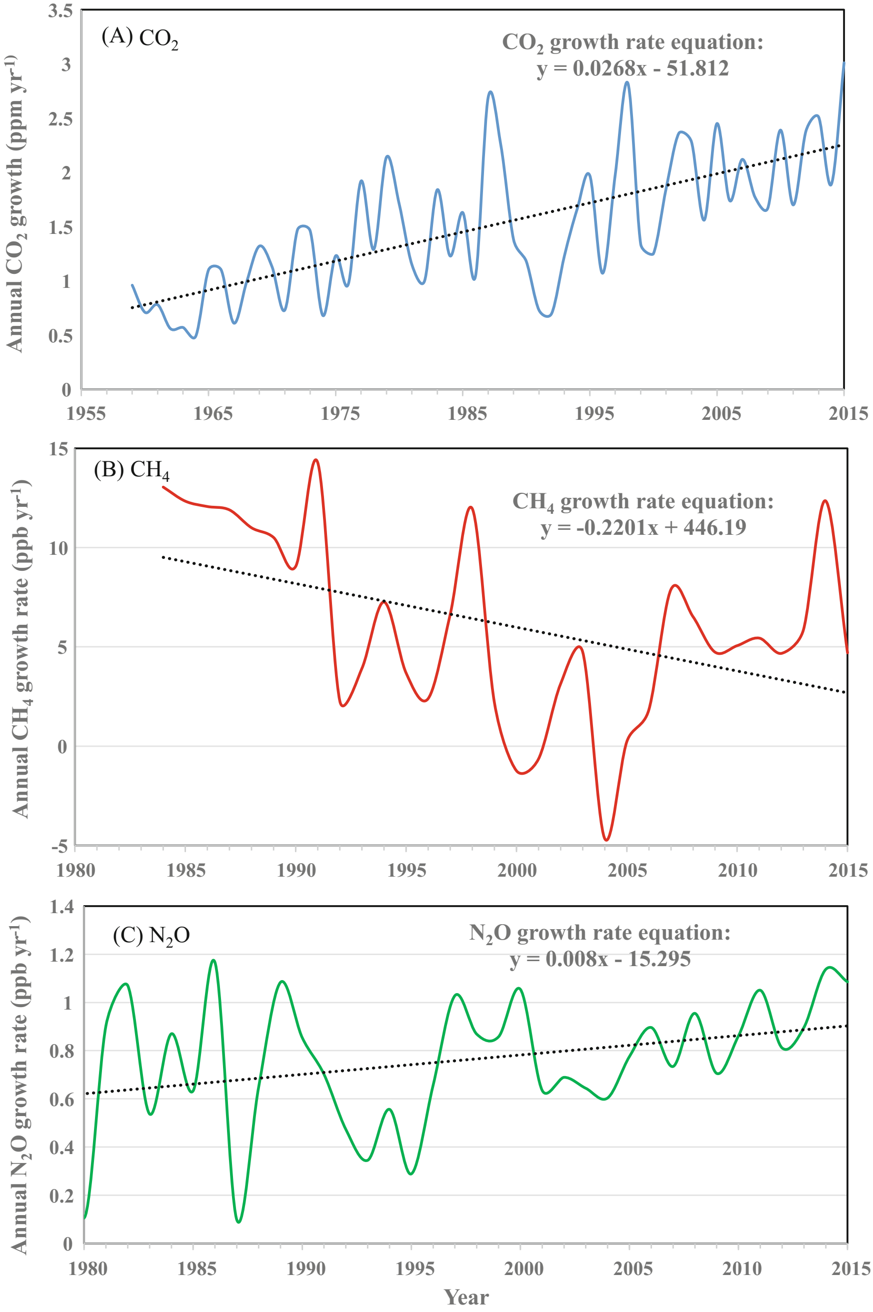

Fig. 2.2 Instantaneous growth rates for globally averaged atmospheric CO_2, CH_4 and N_2O since the instrumental record for each of the major greenhouse gases. Data from NOAA/ESRL

In addition to a well-known anthropogenic greenhouse effect associated with emission of GHGs (e.g., CO_2, CH_4, N_2O, and CFCs) humans also enhance greenhouse effect by emission of pollutants such as CO, volatile organic compounds (VOCs), nitrogen oxides (NO_x), and SO_2. Although these air pollutants are negligible in the atmosphere to cause any significant greenhouse effect, they have indirect greenhouse effect by altering the abundance of important GHGs such as CH_4 and ozone (O_3) through their atmospheric chemical reactions and also acting as precursors of tropospheric O_3 and aerosols formation. They also impact atmospheric OH concentrations as well as CH_4 atmospheric lifetime (Hartmann et al. 2013). The main sources of atmospheric CO are direct emission from incomplete combustion of biomass and fossil fuels, as well as in situ production by oxidation of CH_4. As a result, the atmospheric chemistry and climate change tend to be intrinsically linked. Humans also affect water budget of the planet by changing land surface, resulting into redistributing latent and sensible heat fluxes. Land use changes such as conversion of forests to cultivated land, changes in characteristics of vegetation, change in land surface color through burning, etc. changes reflectivity of the land (i.e., surface albedo), and also the rates of evapotranspiration and IR emissions.

2.4.1 Signs of Changing Climate

Natural forcings have contributed to climate change in past, such as glacial-interglacial cycles. However, the observed climate change in post-Industrial Era, and especially since 1950s has been attributed to other external changes, especially the change in composition of the atmosphere during the industrial period as a result of anthropogenic activities. Many aspects of the global climate are changing rapidly, and there is a wealth of observational evidence that climate is changing, such that warming of the climate system in recent decades is unambiguous. The IPCC in their recent assessment (AR5) concluded that "…warming of the climate is unequivocal, and since the 1950s many of the observed changes are unprecedented over decades to millennia. The atmosphere and ocean have warmed, the amount of snow and ice have diminished and sea level has risen" (p 40, Synthesis Report, IPCC 2014). The atmospheric CO_2 and CH_4 concentrations depart from Holocene and even Quaternary patterns from 1850 with more markedly changes from 1950, with the associated fall in $\delta^{13}C$ as captured by tree rings and calcareous fossils (Waters et al. 2016).

Although the warming of the Earth's surface is the most cited evidence of the climate change, wide range of observations and lines of evidence for climate change exist. These includes: (i) atmospheric surface: air temperature, precipitation, air pressure, water vapor, wind speed; (ii) Atmospheric upper air: earth radiation budget, temperature, atmospheric water vapor, wind speed and direction, cloud properties; (iii) atmospheric composition: GHGs, ozone, other long-lived gases, aerosols and their precursors; (iv) ocean surface: temperature, salinity, sea level, sea ice, ocean current, phytoplankton, CO_2 uptake, ocean acidity, nutrients, oxygen concentration; (v) ocean subsurface: temperature, salinity, subsurface water current, C composition; (vi) terrestrial: snow cover, albedo, permafrost, glaciers and ice caps, photosynthetically active radiation, water use efficiency (WUE), land cover, changes in hydrological cycle—soil moisture, river discharge, ground water (Hartmann et al. 2013; Arndt et al. 2015). Observational evidence of changing climate system has been obtained from multiple independent climate indicators, from the top of atmosphere to the depths of oceans. It includes the cooling of lower stratosphere, warming of lower troposphere, warming of the Earth and ocean surface, and increasing heat content of the ocean. Other changes include those in ocean temperatures, glaciers, snow cover, sea ice, sea level, and atmospheric water vapor (Arndt et al. 2015).

The global land temperatures at the surface, in the troposphere (i.e., the active weather layer extending about 8–16 km above the surface) and in the oceans have all increased in recent decades. The global land surface air temperatures has increased over the period of the instrumental record with warming rates approximately doubling since 1979 (Fig. 2.3a). Together with record-high GHG concentrations, the annual global surface temperature is currently the highest it has ever recorded for the period of 135 years of modern record keeping (Arndt et al. 2015). Several independently analyzed global and regional land surface air temperature (LSAT) data show only minor perturbations to global LSAT records since 1900, and revealed consistently increasing decadal LSAT anomaly trend (Table 2.2; Jones 2016). Furthermore, changes in surface atmospheric specific and relative humidity over the period are physically consistent with the reported global observed temperature trends (Peterson et al. 2011; Simmons et al. 2010).

The global average sea surface temperatures (SST) have increased since the beginning of the 20th century, as revealed by records obtained by different measurement methods (Fig. 2.3b; Kennedy et al. 2012). Although prominent spatiotemporal structures such as El Ninõ South Oscillation (ENSO) and decadal variability patterns in the Pacific Ocean exist, since 1950, SST has increased in all latitudes over each ocean. Different methods have been used to monitor SST over time, including moving ships, buckets, and satellite monitoring, and interpolation of the existing data by modeling. Analysis of these independently collected data show consistently increasing decadal SST anomaly trend (Table 2.2).

The global combined mean land surface and ocean surface temperature (GMST) has increased, with the last 50 years at almost double the rate of the last 100 years (Fig. 2.3c; Jones et al. 2012b; Morice et al. 2012). The GMST calculated by a linear trend has revealed a warming of about 0.85 °C (0.65–1.06 °C) from 1880 to 2012 and almost the whole globe has experienced surface warming with some decadal inter-annual variability (Hartmann et al. 2013). From 1980 each decade has been significantly warmer at the Earth's surface than the preceding decade (Table 2.2). Warming in the last century has occurred in two phases (Fig. 2.3c): (i) from 1910 to 1940s by about 0.35 °C, and (ii) more strongly from 1970s to present by about 0.50 °C. The past three decades have been warmer than all previous decades in the instrumental record. Also, World Meteorological Organization (WMO) identified

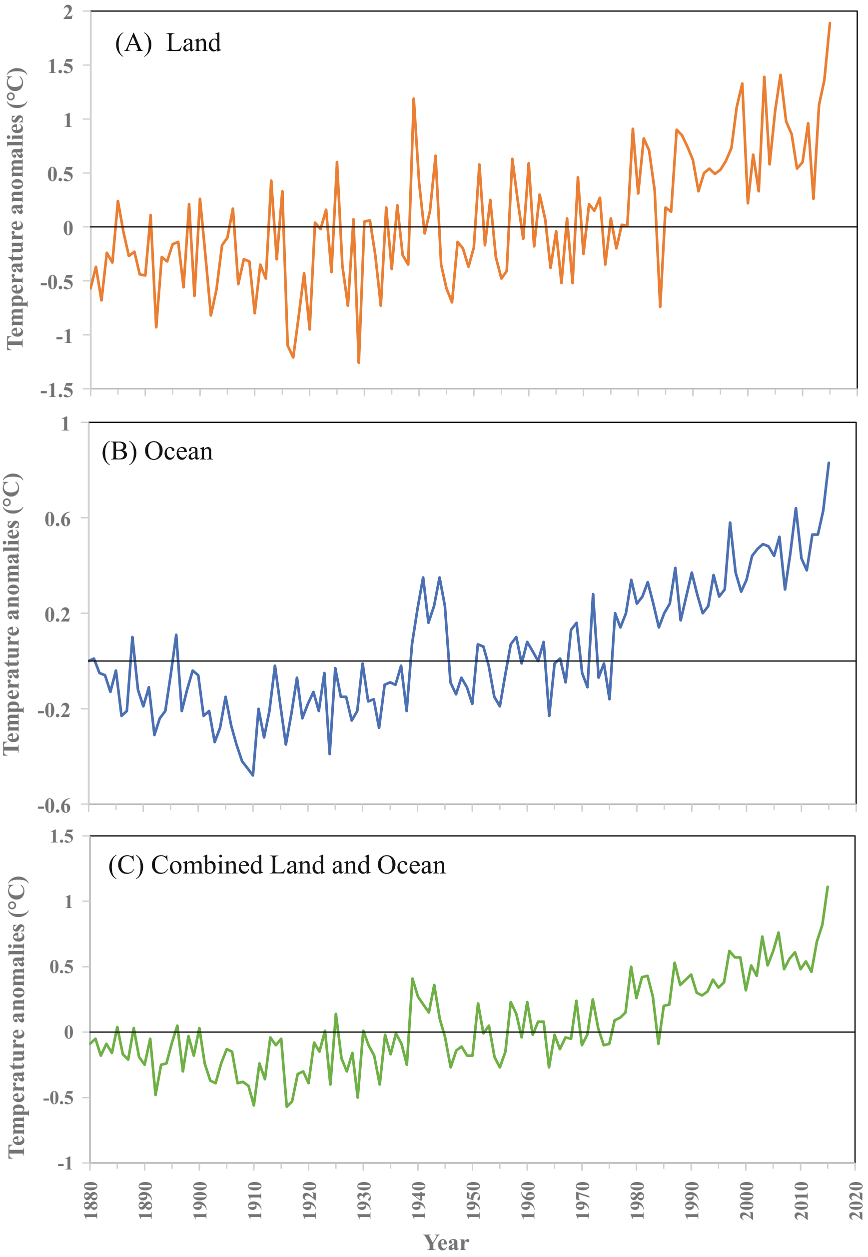

Fig. 2.3 Global annual temperature anomalies from 1880 to 2015. Data source: https://www.ncdc.noaa.gov/cag/time-series/global

Table 2.2 Trends of estimated land surface air temperatures (LSAT), sea surface air temperature (SSAT) and combined land and sea surface temperature (i.e., global mean surface temperature (GMST).

Dataset	Reference	Temperature anomaly trend in °C decade^{-1}				
		1880–2012	1901–2012	1901–1950	1951–2012	1979–2012
Land surface air temperature (LSAT)						
CRUTEM4	Jones et al. (2012b), Jones (2016)	0.086 ± 0.015	0.095 ± 0.020	0.097 ± 0.029	0.175 ± 0.037	0.254 ± 0.050
GHCN	Lawrimore et al. (2011)	0.094 ± 0.016	0.107 ± 0.020	0.100 ± 0.033	0.197 ± 0.031	0.273 ± 0.047
GISS	Hansen et al. (2010)	0.095 ± 0.015	0.099 ± 0.020	0.098 ± 0.032	0.188 ± 0.032	0.267 ± 0.054
Barkeley	Rohde et al. (2013)	0.094 ± 0.013	0.111 ± 0.034	0.111 ± 0.034	0.075 ± 0.029	0.254 ± 0.049
Sea surface temperature (SST)						
HadSST3	Kennedy et al. (2011), Atkinson et al. (2014)	0.054 ± 0.012	0.067 ± 0.013	0.177 ± 0.028	0.074 ± 0.027	0.124 ± 0.030
HadSST2	Rayner et al. (2006), Gil-Alana (2015)	0.069 ± 0.015	0.069 ± 0.012	0.084 ± 0.055	0.098 ± 0.017	0.121 ± 0.033
HadISST	Rayner et al. (2003)	0.042 ± 007	0.052 ± 0.007	0.067 ± 0.024	0.064 ± 0.015	0.072 ± 0.024
COBE-SST	Ishii et al. (2005)	–	0.058 ± 0.007	0.066 ± 0.032	0.071 ± 0.014	0.073 ± 0.020
ERSST	Smith et al. (2008)	0.054 ± 0.015	0.071 ± 0.011	0.097 ± 0.050	0.088 ± 0.017	0.105 ± 0.031
HadSST3	Kennedy et al. (2011)	0.054 ± 0.012	0.067 ± 0.013	0.117 ± 0.028	0.074 ± 0.027	0.124 ± 0.030
Global mean surface temperature (GMST)						
HadCRUT4	Morice et al. (2012), Jones (2016)	0.062 ± 0.012	0.075 ± 0.013	0.107 ± 0.027	0.106 ± 0.027	0.155 ± 0.033
NCDC	Vose et al. (2012), Jones (2016)	0.064 ± 0.015	0.081 ± 0.013	0.097 ± 0.010	0.118 ± 0.021	0.151 ± 0.037
GISS	Hansen et al. (2010)	0.065 ± 0.015	0.083 ± 0.013	0.090 ± 0.034	0.124 ± 0.020	0.161 ± 0.033

the year 2015 as the hottest on record, breaking all previous records by a margin of 0.76 ± 0.1 °C above the 1961 to 1990 average, and for the first time, 2015 temperatures were 1 °C above the preindustrial era. In addition, years 2011–2015 were the warmest 5-year period on record (WMO 2015). Many extreme weather events, including heat waves which influences climate were also observed during this 5-year period.

The data show tropospheric warming in tropics, southern and northern hemispheres from 1958 to 2014 (Haimberger et al. 2012; Sherwood and Nishant 2015; Arndt et al. 2015) suggesting that atmospheric warming that has kept pace with global surface warming, while the stratosphere has been cooling during the same period (Santer et al. 2013; Sherwood and Nishant 2015; Arndt et al. 2015). The observed cooling in the stratosphere, while troposphere and global surface is warming is a fingerprint that the observed warming is due to increase in heat-trapping GHGs. In contrast, if the observed warming had been due to increases in solar output, Earth’s atmosphere would have warmed throughout—global surface, troposphere and stratosphere (Santer et al. 2013, 2014). Other aspects climate, including changes in precipitation patterns (Min et al. 2011; Pall et al. 2011; Stott et al. 2016; Liu et al. 2016), increasing humidity (Santer et al. 2007; Willett et al. 2007; Mondal and Mujumdar 2015), change in pressure (Gillett and Stott 2009; Stott et al. 2016), and increase in heat content of the ocean (AchutaRao et al. 2006).

Natural drivers of climate cannot explain the observed warming, since over the last five decades, natural climate factors—such as solar forcing and volcanic eruptions—alone would have led to slight cooling (Gillett et al. 2012). The majority of the warming at the global scale over the past fifty years can only be explained by the anthropogenic influences, especially emissions from fossil fuels combustion (Santer et al. 2013; Stott et al. 2010). Consistent with scientific understanding of polar amplification of surface air temperature variations (Bekryaev et al. 2010), the largest increases in temperature are occurring close to the poles especially in the Arctic, and it is causing significant snow and ice cover to decrease in most areas, including Arctic sea, while atmospheric water vapor is increasing, since warmer atmosphere can hold more water. Global sea levels are also rising. Averaged over the recent decades, the sea levels are substantially different than they were half a century earlier.

Globally averaged surface air temperature has slowed its rate of increase since late 1990s (Fig. 2.3) even though each decade has been warmer than the previous. The slower recently observed rates of global surface warming from 2009 to 2012 which has been referred to as ‘*warming hiatus*’ (Fig. 2.3) has been attributed to combination of factors, including cooling effects from natural radiative forcing (Santer et al. 2014), and energy redistribution within the ocean due to unforced variability (Palmer and McNeall 2014). It is estimated that more than 90% of increase in energy of the climate system between 1971 and 2015 has accumulated in oceans (Levitus et al. 2012; NOAA 2016), which goes towards warming the ocean (Abraham et al. 2013) and only about 1% of energy is stored in the atmosphere. Globally, the upper 0–75 m depth of the ocean water warmed by an average of 0.11 ± 0.2 °C decade^{-1} over the period 1971–2012 (Levitus et al. 2012). The amount of heat accumulating in ocean plays vital role for diagnosing Earth's energy imbalance and sea level rise. Over the past four decades, the process of ocean heat uptake has resulted in marked increase in upper ocean heat content and ocean thermal expansion, thus contributing to sea level rise (Hanna et al. 2013). The ocean heat acts as buffer to climate change by slowing the rate of surface warming. The top 700 m depth ocean heat uptake from 1970 is estimated at 19×10^{22} J, which implies an average ocean water warming of 0.2 °C for the 43-year period (Abraham et al. 2013). The global sea level rise attributed to thermal expansion is 3 mm yr^{-1} over the past 20 years (Abraham et al. 2013).

Cumulative CO_2 emissions from fossil fuels combustion, cement production, and land use change during the Industrial Era (1750–2015) is estimated at 600 ± 55 Pg C, of which, 260 ± 5 Pg C or ~43% remained airborne (Le Quéré et al. 2015, 2016), resulting into ~122 ppm increase or a relative abundance of ~144% compared to the 1750 atmospheric concentrations (WMO 2016). An estimated 175 ± 20 Pg C or ~29% was taken up by the global oceans, while the remaining balance is believed to be retained in the terrestrial sinks (Le Quéré et al. 2015, 2016). Enhanced ocean uptake of CO_2 alters the marine $CO_3{}^{2-}$ system that controls sea water acidity. Oceans have absorbed 25–30% of the anthropogenic CO_2 emissions since the beginning of the industrial revolution. Although oceans act as C sinks, the CO_2 absorption process has a direct and measurable impact on ocean chemistry. Since late 18th century, the average pH of surface waters has decreased by 0.1 units, from 8.2 to 8.1, which is equivalent to 30% increase in H^+ concentration (Logan 2010). Changes in ocean chemistry affects marine life by (i) affecting calcification process of calcifying organism e.g., corals, (ii) decreasing pH which affects acid-base regulation and other physiological processes in the ocean, and (iii) increasing dissolved CO_2 which could affect the ability of primary producers to photosynthesize. Ocean surface has been more impacted with CO_2 uptake than the deep ocean. The observed change in ocean chemistry that indicates that the uptake of CO_2 has led to a reduction of the pH of surface seawater by 0.1 units, equivalent to a 30% increase in the concentration of H^+ is dominantly associated with surface and near surface waters (Raven et al. 2005). Similarly, there are indications that, parallel to increase in acidity and ocean water warming, O_2 concentration has decreased in coastal waters, open ocean thermoclines since 1960s, with likely expansion of tropical O_2-minimum zones in recent decades.

In addition to observed increase of the land and sea surface temperature in the last 100 years (Fig. 2.3), over the last 30 years, satellites have made it possible to observe much broader spatial distribution of measurements, and indicate that upper ocean temperature has increased since at least 1950 (Willis et al. 2010; Lyman et al. 2010; Roemmich et al. 2015). Observations from satellites and also in situ measurements have suggested reductions in glaciers, Arctic sea ice and ice sheets (Holland and Kwok 2012; Matear et al. 2015). In addition to imbalances in radiation budget discussed in Chap. 1, satellite datasets based on measurements of electromagnetic radiations suggest small imbalance in heat content of the ocean (Hartmann et al. 2013). Atmospheric water vapor is also increasing in the lower atmosphere, because warmer atmosphere can hold more water. Changes in average conditions have been accompanied by increasing trends in extremes of heat and heavy precipitation events and decreases in extreme cold (Alexander et al. 2006). It has been predicted that a doubling of the Earth's atmospheric CO_2 concentration from preindustrial concentration would warm Earth's surface by an average of between 1.5 and 4.5 °C (Kiehl 2007; IPCC 2013). Globally, GHGs emissions have been increasing as the growing demand for energy has more than offset the progress made in improved energy efficiency and deployment of new energy sources with lower GHG emissions. Natural drivers of climate cannot explain the current observed warming.

The ability to predict manifestations of changing climate carries considerable uncertainties suggesting that it is quite possible that the climate change impacts may be considerably worse in the near future than predicted. One of the examples is the reduction in Arctic perennial ice sheet, which has diminished at a rate of 13% per decade relative to previous mean rate from 1979 to 2012 (Stroeve et al. 2012b), which far exceeded model predictions (Stroeve et al. 2012a) and serve as indication that climate change impacts may occur rather sooner than expected. A number of other manifestations of the changing climate have been also observed, including rising sea level, drought, heat waves, more severe storms, increasing precipitation intensity, and associated disruption of terrestrial and aquatic ecosystems. In addition, increased atmospheric CO_2 concentration is diffusing into the ocean and acidifying surface waters and affecting marine ecosystems. Natural processes are currently removing less than half of anthropogenic CO_2 emissions from the atmosphere each year.

2.4.2 Climate Change Metrics

Efforts to mitigate anthropogenic climate change need to be able to assess the relative effectiveness of measures addressing the different forcing agents. Metrics are used in studies of climate change to simplify interpretation of the complex feedbacks and interactions that determine the ultimate effect of forcings. Various metrics of climate influence have been developed, each with its advantages and disadvantages. A climate change metric, generally is a variable or set of variables designed to parameterize a set of known or deduced influences on climate system that may result in climate change. The climate metrics is then used as a proxy to indicate the impact of forcing on the climate system resulting in change in energy balance of the Earth-Atmosphere system.

The potential uses of climate metrics include: (1) providing rapid evaluations of multiple potential approaches proposed to minimize the impact of anthropogenic activities on the climate system, (2) evaluation of relative contribution of two or more emissions from different anthropogenic activities to climate change, (3) evaluation of climate effects of competing technologies or energy usage and contributions of different emissions, (4) establishment of a basis for comparing changes in climate effects in different countries or regions, (5) evaluation of proposed policies that encourage beneficial activities or discourage non-beneficial activities, (6) help industries or countries determine the best approaches and practices to meet specific commitments to reduce climatic impacts, and (7) quantification of the relative contributions of countries (Ravishankara et al. 2015). Some of required key features of a metric include: (i) scientifically sound, and also simple to use and easy to understand and communicate, (ii) applicable to scientific questions or policy issues of interest to the user, (iii) useful as a tool for communicating impact information among scientists, industry, and policy makers, (iv) transparent enough to convey the intended information by itself, and (v) simple, but creating confidence in the scientific integrity and trust of the metric. Among the various metrics, the more well-known are Global Warming Potential (GWP) and Global Temperature change Potential (GTP).

2.4.2.1 Global Warming Potential

Each GHG differs in its atmospheric lifetime and radiative efficiency (i.e., how effectively a gas absorbs and re-radiates IR). The GWP is the most commonly used metric for comparing the RF of gases at different lifetimes, radiative characteristics and gas cycling. Using the GWP, GHG fluxes are converted to a common unit of 'CO_2 equivalents' and then compared directly to one another to determine whether ecosystem has a net warming or cooling effect on global climate. The GWP is defined as time-integrated RF due to pulse emission of given component, relative to a pulse emission of an equal mass of CO_2. In other words, for the a given GHG, it is an index measuring RF following a pulse emission of a unit mass of a GHG in the present day atmosphere integrated over a chosen time horizon, relative to that of CO_2. The GWP represents the combined effect of the differing times these gases remain in the atmosphere and their relative effectiveness in causing RF. Since GWP is a time integrated index, its value changes depending on the timescale of interest. The Kyoto protocol is based on GWPs from pulse emissions over 100-year time frame. The ecosystem ecologists and climatologists are interested in near term climate change, and therefore, most GHG calculations uses 100-year time frame. A direct interpretation of the existing definition is that GWP is an index of total energy added to the climate system by a component in question relative to that added by CO_2. However, the GWP does not lead to equivalence with the temperature change or other climate variables due to differences in the atmospheric lifetimes of the gases (Daniel et al. 2012). Thus, the name GWP may be somewhat misleading, and relative cumulative forcing index may be more appropriate term (Myhre et al. 2013). The GWP is generally used as a default metric for transferring emissions of different gases to a common scale, often called 'CO_2 equivalent emissions'. The GWP of a component i is expressed as [Eq. 2.2]:

$$GWP_i = \frac{\int_0^{TH} RF_i(t)dt}{\int_0^{TH} RF_r(t)dt} = \frac{\int_0^{TH} a_i.[C_i(t)]dt}{\int_0^{TH} a_r.[C_r(t)]dt} = \frac{AGWP_i}{AGWP_{\mathrm{CO_2}}} \tag{2.2}$$

where, *TH* is the time horizon, (i.e., 20, 100, or 500 year horizon), RF_i is the global mean RF of component *i*, *ai* is the RF per unit mass increase in atmospheric abundance of component *i* (i.e., radiative efficiency) $[C_i(t)]$ is the time dependent abundance of *i*, and corresponding quantities for the reference gas *(r)* in the

Table 2.3 Strengths and limitations of global warming potential (GWP) and global temperature change potential (GTP)

Global warming Potential (GWP)	Global temperature change potential (GTP)
STRENGTHS	
• The concept is easy to understand • The concept is easy to calculate • It is successful at transforming various GHGs to a common unit (CO2 equivalent) • It performs time integration of radiative forcing (RF) to project climate change to some future time • It can be modified to include equivalent forcing using efficacies • It is widely used in existing policy	• The concept is relatively simple and transparent • The concept requires few input variables • It allows calculation of time-dependent change in temperature which GWP does not allow
LIMITATIONS	
• It only considers effects for which RF is calculated • It does not evaluate the temperature change or time evolution of temperature change • Time integration of RF is not clearly defined • Comparison of short-lived or non-homogenous forcing is difficult (same problem for all existing metrics) • It incorporates all the limitations inherent in RF except that of atmospheric lifetime that is fully accounted for • Characterization of the impact of gas is not robust with respect to the climate impact • It is not a stable metric, GWP values have changed over time due to rapid improvements in understanding of the C cycle • It is difficult to what an appropriate time horizon should be, although the 100 -year has become the standard • It is less applicable in traditional configuration for fixed target policy analysis	• It may be limited to sustained emission applications • More studies of pulse emission effects are needed to assess its effectiveness • It depends on numerical value of climate sensitivity which is not well known • There is no clear choice on how to define equivalence • Similar to GWP and other emissions-based metrics, it is difficult to include non-emission-related effects including those occuring with formation of contrails

denominator (Forster et al. 2007), *AGWP* is absolute global warming potential for gas *i* or CO_2. The AGWP is calculated by integrating the RF due to emission pulses over a chosen time horizon (i.e., 20 and 100-year). It can have advantages for certain applications because AGWPs are not dependent on comparisons with CO_2. Comparison with CO_2 may not always be desired in some emissions (e.g., comparisons of NO_x emission effects from aviation relative to NO_x emissions from ground-based transportation systems).

GWP is a better measure of relative effects on climate than the comparison of RFs for different gases because GWPs differentiate between gases that would reside in the atmosphere for vastly different amount of times from few days to several centuries (Ravishankara et al. 2015). The GWP is approximately equal to the ratio of temperature response due to a sustained emission of species or the integrated temperature response for a pulse emission normalized to similar expression for CO_2 (Azar and Johansson 2012; Ravishankara et al. 2015). Strengths and limitations of GWP are summarized in Table 2.3. Multiplying the mass of gas [in megagrams (Mg)] by the associated 100-year GWP derives the CO_2 equivalent for a gas.

2.4.2.2 Global Temperature Change Potential

An alternative to GWP that has received considerable attention recently is the Global Temperature change Potential (GTP), a metric that evaluates the cause-effect, and is defined as the change in global mean surface temperature at a selected point in time response to an emission pulse relative to that of CO_2 (Neubauer and Megonigal 2015; Shine et al. 2005). Although GTP has received much attention as alternative to GWP, it has not yet been used for policy decisions. GTP gives the temperature changes as a function of time rather than that of integrated over certain time. GTP which was proposed by Shine et al. (2005), derive the relative temperature increase per unit mass of emission of GHG relative to that for an equivalent mass of emitted CO_2 for a chosen integrated time horizon. GTP can be defined as either a pulse (GTP_p) or a sustained emission (GTP_s) can be used for calculating GTP (Shine et al. 2005). The GTP concept is based on assumption that the global mean surface temperature can be defined based on change in RF and heat capacity (C) as (Eqs. 2.3, 2.4):

$$\Delta T(t) = \frac{1}{C}\int_{0}^{t} \Delta F(t')\exp\left(\frac{t'-t}{\lambda C}\right) \tag{2.3}$$

or:

$$C\frac{d\Delta T(t)}{dt} = \Delta F(t) - \frac{\Delta T(t)}{\lambda} \tag{2.4}$$

where, ΔT is the change in temperature as a function of time, ΔF is change in RF, C is the heat capacity of the mixed layer ocean, λ is the assumed climate sensitivity, the exponential is an impulse response function to forcing at some initial time t' and t is some time in the future. In this equation, it is assumed that ocean and land respond together and at the same rate, and therefore, they are together represented by single heat capacity. This assumption allows the climate system to have single time constant rather than slow time constant (ocean) and fast time constant (land), thus greatly simplifying the calculation.

For a known time-dependent increase or decrease in the concentration (S) of a greenhouse gas, the concentration change over time is expressed as (Eq. 2.5):

$$\Delta X(t) = \alpha \Delta S\left[1 - \exp\left(\frac{t}{\alpha}\right)\right] \tag{2.5}$$

where α is the time constant for removal of gas x, and for the forcing (F) given by $A\Delta X(t)$, absolute GTP for a sustained emission change ($\mathrm{AGTP_s}$) at a particular integration time for a forcing x is derived by [Eq. 2.6]:

$$AGTP_s^x = \frac{\alpha_x A_x}{C}\left\{\tau\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] - \frac{1}{\tau^{-1} - \alpha^{-1}}\left[\exp\left(-\frac{t}{\alpha_x}\right) - \exp\left(-\frac{t}{\tau}\right)\right]\right\} \tag{2.6}$$

where α is the time constant for removal of the gas x, A is the RF for s 1 kg change in concentration for gas x, C is the heat capacity of the mixed layer ocean, and τ is the time constant (λC) for the climate system. Similar to AGWPs, the AGTPs for CO_2 are more complicated because of the complexity of its removal processes. The resulting GTP as a function of a gas or other forcing agent x is the ratio of AGTP for x divided by AGTP for CO_2 [Eq. 2.7]:

$$GTP_S^x(t) = \frac{AGTP_s^x(t)}{AGTP_s^{CO_2}(t)} \tag{2.7}$$

and like GWP, GTP uses radiative forcing, but calculates the response of the surface temperature to the RF for the emitted gas. GTP is also expressed as a relative change for a gas compared to CO_2, [Eq. 2.8]

$$GTP_i(t) = \frac{AGTP_i(t)}{SGTP_{CO_2}(t)} = \frac{\Delta T_i(t)}{\Delta T_{CO_2}(t)} \tag{2.8}$$

Therefore, GTP accounts for the thermal inertia and response of the climate system to provide a relative measure of temperature responses for specific time horizon. The strengths and limitations of GTP and GWP as climate matrices are compared and contrasted in Table 2.3. The GTP for various gases can be used to relatively weigh the effects of different emissions to obtain ‘CO_2 equivalents’ similar to those of GWPs. However, the concepts for constructing GWPs and GTPs are fundamentally different. GTPs can account for physically based processes such as climate sensitivity and ocean-atmosphere exchange of heat that cannot be done with GWPs. GTPs can also account for the slow response of the deep ocean and the resulting effects on the temperature response, which in effect prolongs the response from emissions beyond what is controlled by the lifetime of the gas. As a result, GTPs therefore, account for both the atmospheric response time scale of the gas under evaluation as well as response time of the climate system. GTP concept also has inherent uncertainties such as those associated with the climate sensitivity and ocean heat uptake (Table 2.3; Myhre et al. 2013; Olivie and Peters 2013). GTPs tend to have larger uncertainty range compared to the GWPs determined for the same gas (Ravishankara et al. 2015). GWPs are an integrated measure of the system, and recent analysis has shown that GWPs are useful measure of the energy entering the climate system (Olivie and Peters 2013), and the derived GWP for a gas depends only on the integral of the RF. While the GTPs saves as an instantaneous measure, the pathway of the forcing following emission of the gas is important (Ravishankara et al. 2015).

2.5 Conclusions

The global climate is changing, and the change is apparent across a wide range of observations, including global temperature increase and sea level rise. The global warming of the past century is primarily attributed to human activities during the Industrial Era, and the global climate is projected to continue to change over this century and beyond. The magnitude of observed climate change beyond the next few decades depends primarily on the amount of GHGs emitted globally and the sensitivity of Earth’s climate to those emissions. The global abundance of CO_2, CH_4 and N_2O in the atmosphere at the beginning of Industrial Era in 1750 were 278 ± 2 ppm, 722 ± 25 ppb, and 270 ± 7 ppb for CO_2, CH_4 and N_2O, respectively, and increased to 400.0 ± 0.1, 1.845 ± 0.002, and 0.328 ± 0.0001 ppm in 2015 for CO_2, CH_4 and N_20, respectively. Mean annual absolute increase during the last decade is estimated at 2.08 ppm yr^{-1}, 6.0 ppb yr^{-1}, and 0.89 ppb yr^{-1} for CO_2, CH_4, N_2O, respectively. The globally averaged combined land and ocean surface temperature revealed a warming of 0.65–1.06 °C for the period 1880 to 2012, and the global average surface temperature in 2015 reached a symbolic and significant milestone of 1 °C above the pre-industrial era. In addition to global temperature, a wide range of climate variables have been monitored, covering the atmosphere, the terrestrial, the ocean and even the paleoclimate records, all pointing to the fact that the global climate is changing, with significant global warming, and the human activities have contributed significantly to these changes. The most notable anthropogenic activity is the combustion of fossil fuels, which has released an estimated 410 ± 20 Pg C from 1750 to 2015 from geologic reserves, resulting into an atmospheric CO_2 growth of 260 ± 5 Pg C for the same period, together with significant changes in ocean chemistry and heat content. The second significant contributor is the land use conversion and deforestation (Refer Chap. 6). From 1750 to 2015, land use and land conversion and deforestation have released an estimated 190 ± 65 Pg C. The decadal land use emissions during 2005 to 2014 is estimated at 1.0 ± 0.5 Pg yr^{-1}, while the terrestrial C sink is estimated at 3.0 ± 0.8 Pg C yr^{-1}. The decadal CO_2 emissions averaged over the last decade (2006–2015) revealed that 91% of total CO_2 emissions was caused by fossil fuels combustion and industry, whereas land use and land use change contributed 9% of total CO_2 emissions during the last decade. During the last decade, CO_2 emissions partitioned among atmosphere (44%), ocean (26%) and terrestrial land sink (30%).

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Chapter 3
Introduction to Global Carbon Cycling: An Overview of the Global Carbon Cycle

Abstract Carbon (C) is the essential attribute of life. Therefore, its cycling gives the overall index of health of the biosphere. Global C cycling involves the exchange of C between its four main reservoirs—the atmosphere, terrestrial biosphere, oceans and sediments. Understanding the biogeochemical processes regulating the movement of C from one reservoir to another is central to control carbon dioxide (CO_2) and methane (CH_4) emissions and mitigating climate change. This introductory chapter presents an overview of the global C cycle. The atmospheric carbon burden —both CO_2 and CH_4 concentrations, has increased significantly since the beginning of the Industrial Revolution in response to anthropogenic perturbations of the global C cycle. The major sources of the increase in atmospheric C content are the utilization of fossil fuels for energy, cement production, land use conversion and deforestation. Fossil fuel and cement production released 410 ± 20 Pg C between 1750 and 2015. Similarly, land use change released 190 ± 65 Pg C over the same period. The atmospheric C burden increased by 260 ± 5 Pg between 1750 and 2015. The consequences of changes in global C cycling extend beyond the global warming associated changes in radiation balance caused by increased concentration of trace gases. It causes changes in atmospheric photochemistry, disturbances in terrestrial ecosystems as well as marine chemistry and ecosystems. In the following chapters these effects will be discussed in much more details.

Keywords Biosphere · Carbon reservoirs · Methane · Lithosphere · Carbon fluxes · Fossil fuels

Contents

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3.1 Introduction

Carbon (C) in the elemental form occurs as amorphous C, graphite and diamond. The C atoms can change their oxidation state from +4 to −6, and occurs mostly in the +4 state as carbon dioxide (CO_2) and in carbonate ($CO_3{}^{2-}$) form. The CO_2 is a trace constituent in the atmosphere, comprising $\geq 0.04\%$ of all molecules in the atmosphere. Carbonate is present in the lithosphere as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and siderite ($FeCO_3$). In aqueous form, carbonate exists as H_2CO_3, $HCO_3{}^{-}$, and $CO_3{}^{2-}$. Carbon monoxide (CO) is present in the atmosphere as oxidation state +2. The most reduced form of C (−4) is methane (CH_4).

Carbon is a fundamental element for all forms of life on Earth, and is the essential element present in all known life forms, making up $\sim$50% of dry weight of living things. Therefore, estimates of global production and the decomposition of organic carbon (OC) gives the estimate of overall index of health of the biosphere—both past and present. Life requires an energy flow through the biosphere for which the dominant primary energy is solar radiation, and cycling of C through photosynthesis enables energy flow. The cycling of C approximates the flow of energy around the Earth, which include metabolism of natural ecosystems, human, and also industrial systems. Plants transform solar energy to chemical energy in organic C molecules which provide biochemical machinery underlying the evolution and use of environmental energy, the essential attribute of life. The C is one of six elements (C, H, O, N, P, and S) which form major constituents of plant tissue, and life on Earth depends on its cycling through various transformations and transfers among the atmosphere, the oceans, plants and animals, soils, rocks, and sediments at various timescales ranging from seconds (e.g., fixation of atmospheric CO_2 into carbohydrates and other plant biomass through photosynthesis) to geologic timescales (e.g., accumulation of fossil C through the diagenesis processes). C is constantly being absorbed, released, and recycled by a range of natural and human-induced physical, biological, and chemical processes in the biosphere. It also creates atmospheric greenhouse effect (as CO_2), buffers pH in sea water, and its redox buffers many reactions. The various constituents of C interact through biogeochemical cycling, a series of processes that transfers C among reservoirs and transform it among its various molecular forms during its transfers. Therefore, the global C cycling refers to exchange of C within and between array of C reservoirs linked by a network of physical, chemical, and biological processes. The overall C cycle consists of multiple nested cyclic pathways that differ with respect to some of their reservoir processes. The major reservoirs of C are: (i) the atmosphere, (ii) the oceans, (iii) terrestrial land (soil, vegetation), and (iv) lithosphere.

All C cycle pathways ultimately pass through the hydrosphere and atmosphere which is the common course that unites the entire C cycle and allow even its remote constituents to influence both the environment and the biosphere (Des Marais 2001).

Over millions of years, CO_2 is removed from the atmosphere through weathering processes—by silicate rocks and through burial of fixed C by marine plants in the marine sediments (Berner 1998). Chemical weathering, which results in CO_2 sequestration as $CaCO_3$ in sedimentary rocks at warmer Earth temperatures or release CO_2 to the atmosphere if the Earth becomes cold has enabled the Earth's climate to stay within a narrow range of temperatures through the geological timescale (Archer 2010). However, once disturbed, it will take hundreds of thousands of years for the Earth's climate to be restored through its natural C cycle balances.

The principal form of C in the atmosphere is CO_2 and CH_4. These gases have played crucial and distinct roles in the development of life forms and alteration of Earth's surface environment throughout the Earth's history. CO_2 is the principal medium of photosynthesis, metabolism and organic material decomposition. Through its transformation in weathering and CO_3^{2-} precipitation it supplies a large portion of the C cycling through the lithosphere. CO_2 is also the dominant long-lived greenhouse gas (GHG) contributing to climate forcing. Since 1750, its radiative forcing has increased by 1.94 W m^{-2} or ~65% of the increased forcing by all long-lived GHGs (NOAA 2015). Systematic atmospheric CO_2 concentration measurements began at Mauna Loa Hawaii in 1958 and established the annual mean mole fraction of 315 ppmv in 1958. The daily averaged CO_2 concentration at Mauna Loa exceeded 400 ppm for the first time in May 2013 (Fig. 3.1).

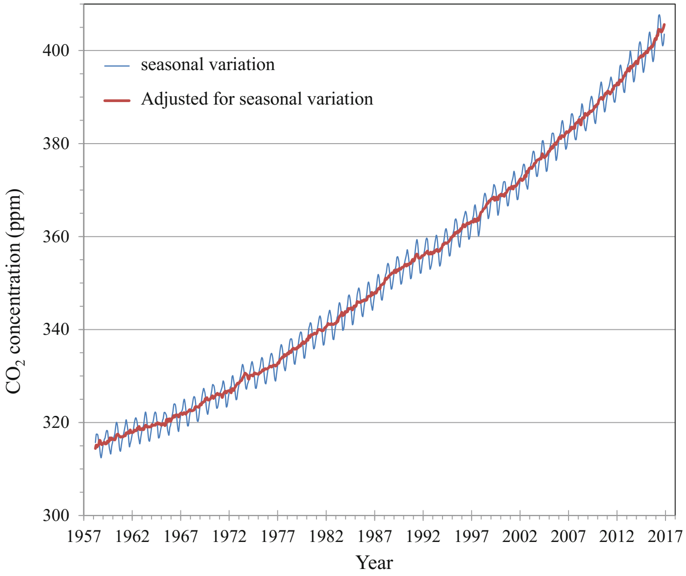

Fig. 3.1 Carbon dioxide measured at Mauna Loa, Hawaii

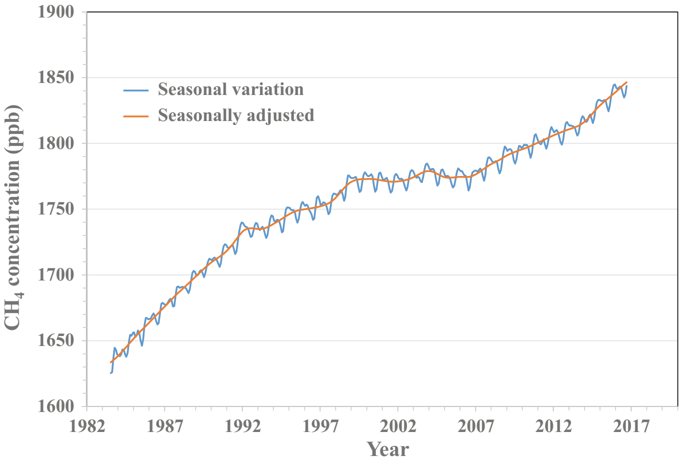

Fig. 3.2 Globally averaged dry air CH_4 mol fraction from 1983 to 2016 (data from NOAA/ESRL)

The atmospheric CH_4 has contributed ~0.5 W m^{-2} direct radiative forcing since 1750. Indirect effects from the production of tropospheric ozone (O_3) and stratospheric H_2O added another ~0.2 W m^{-2} making a total CH_4 radiative forcing of 0.7 W m^{-2} (NOAA 2015). Atmospheric CH_4 is produced by both natural (40%) and anthropogenic sources (60%). Atmospheric CH_4 has increased by about a factor of more than 2.5 since the pre-industrial era. The annual rates of increase of 10 ppb yr^{-1} in the 1980s slowed dramatically to near zero in the early 2000s' then jumped to 0.6 ppb yr^{-2} in 2007 and remaining steady since (Fig. 3.2). The CH_4 represents the anaerobic side of C cycling through microbial metabolism and release from organic matter (OM) trapped in rocks and sediments. The major transfers of C mass in the C cycle are usually associated with CO_2 through atmosphere where the atmosphere acts as a clearing station linking major C flows among its major reservoirs. However, CH_4 may have played a more important role in the past and is considered a more sensitive indicator of changes in Earth's processes. Both CO_2 and CH_4 are the primary compounds through which C cycling over all timescales has influenced the Earth's surface.

3.2 Photosynthesis and Respiration

Photosynthetic organisms take up CO_2 from the atmosphere and utilize sunlight energy to convert it to biomass as they grow, which animals and human beings use the generated biomass for food, shelter, and energy which fuels the biosphere. Therefore, photosynthesis is important fundamental process in which plants absorbs atmospheric CO_2 and also convert solar energy to chemical energy and store it in plants. When they die and decompose, the C contained in its biomass is transformed into soil organic matter (SOM), which is critical in conditioning soil quality and CO_2 production. Emissions from natural systems and anthropogenic activities return C to the atmosphere, which renews the cycle. Photosynthesis is also important for production of molecules of O_2 in the atmosphere. Thus, the C and oxygen cycles are intricately linked and the presence of O_2 in the Earth's atmosphere sets the redox potential for organic metabolism in ecosystem. The terrestrial ecosystems photosynthetic productivity changes in response to changes in temperature, precipitation, atmospheric CO_2 concentration, and plant nutrients supply. If climate changes to become more favorable for growth, productivity increases and C uptake from atmosphere is enhanced, and vice versa.

3.3 Timescales and Modes of the Carbon Cycle

The global C cycle can be viewed as a series of reservoirs of C in the Earth System which are connected by exchange fluxes of C. Two domains of C in the global cycle distinguished by the turnover rates are (i) fast turnover domain with large exchange fluxes and rapid reservoir turnovers consisting of the atmosphere, land vegetation, soils, and fresh waters, ocean, surface sediments in the ocean—with turnover ranging from few years to millennia, and (ii) slow turnover domain consisting of large pool of C in rocks and sediments with turnover in geological time—1,000,000 years or longer. The exchange of C between slow and fast domain occur only through chemical weathering, erosion and sediment formation in the ocean (Sundquist 1986). More detailed accounts on slow and fast turnover domains of C cycle are presented in Chaps. 5 and 6, respectively. The natural exchange fluxes between faster and slow domains are relatively small <0.3 Pg yr^{-1} (Pg C = Petagram C = 10^{15} g), and can be assumed to be constant over a timescales of centuries unless modified by human induced changes (Raymond and Cole 2003). Prior to Industrial Era, the fast domain was close to steady state with relatively small variations in atmosphere CO_2 and CH_4. However, fossil fuel combustion since the beginning of Industrial Era has transferred large quantities of C from slow domain to fast domain, resulting into significant and unprecedented anthropogenic perturbation of the global carbon cycle.

The biogeochemical C cycle involves abiotic and biotic processes, and transfers C within and between four major reservoirs—the lithosphere (i.e., the solid outer crust), the hydrosphere (i.e., the aqueous envelope of water bodies), the atmosphere and the biosphere linked by a complex set of natural and anthropogenic biogeochemical processes. The amount comprised in individual reservoirs illustrates their principal impact on the global cycle. The principal C emitter carrier in the C cycle is CO_2, and in the absence of anthropogenic influence, C cycle is generally in a steady state. Carbon exchange between individual reservoirs involves photosynthesis, respiration, gas exchange through the water-atmosphere interface and weathering. The C cycle has never been stable at any time in Earth's history.

Over geologic timescales, natural changes in the balance of fluxes in the global C cycle have caused past variations in atmospheric CO_2 concentrations, which has been associated with past changes in climate—such as the periods of expanded continental glaciation (i.e., ice ages) during the last several hundred thousand years which were associated with lower atmospheric CO_2 concentrations (Petit et al. 1999; Lüthi et al. 2008). Although the atmospheric CO_2 is just one of the many factors considered to have affected climate change over the course of Earth history, the existing geologic record is consistent with current understanding of the radiative contribution of CO_2 and CH_4 to the current and historic climate.

Mankind is altering these processes by transforming areas of natural vegetation to human use in agriculture, forest, and urbanization which has vastly changed Earth's land cover and redirect large quantities of global net primary productivity (NPP) to the production of food, fuel, clothing, and shelter (Haberl et al. 2007). The net result of human activities is to increase the release of CO_2 to the atmosphere.

The CO_2 moves between the atmosphere and ocean by molecular diffusion when there is a CO_2 gas pressure (pCO_2) gradient between atmosphere and the ocean. Based on large quantities of measurements of the global surface water pCO_2 since 1960's (Takahashi et al. 2002), a net decadal uptake of 2.2 ± 0.5, 2.3 ± 0.5, and 2.6 ± 0.5 Pg C yr^{-1} has been estimated for the 1990–1999, 2000–2009, 2006–2015, respectively, and an uptake of 3.0 ± 0.5 Pg C yr^{-1} is estimated for 2015 (Le Quéré et al. 2015, 2016).

The C cycle encompasses many processes, including the daily cycling of animal feeding and metabolism, the seasonal cycle of plant growth and decay, and geologic cycle of sediment burial and weathering, and all these processes are linked to the exchange of CO_2 with the atmosphere. The C cycling operates all life forms, inorganic C, organic C reservoirs, and links between them.

3.4 Introduction to Carbon Budget

The C budget is an accounting of the balances of exchanges of C among the reservoirs (i.e., how much is coming in from other reservoirs and going out at a particular time). When the inputs (i.e., the sources) to the reservoir exceed output (i.e., the sinks) the amount in reservoir increases. The cycling determines the budget observed at any particular time. The global C budget is currently out of balance, with C accumulating in the atmosphere in the form of CO_2 and methane (CH_4) since the beginning of industrial era—circa 1750.

The global mean atmospheric CO_2 concentration has increased by over 40% from approximately 278 parts per million (ppm) in 1750, the beginning of the Industrial Era at first slowly and then progressively faster (Etheridge et al. 1996; Joos and Spahni 2008) reflecting the pace of global industrial development, fossil fuel combustion, population growth, and agricultural expansion. The current atmospheric concentration is 400.0 ± 0.1 ppm by the end of 2015 (WMO 2016) the highest level measured in the past 800,000 years (Lüthi et al. 2008). These changes have been known from well-replicated measurements of the composition of air bubbles trapped in Antarctic ice. Atmospheric CO_2 concentration have been measured directly with high precision since 1957, and these measurements agree with ice core measurements and show a continuation of the increasing trend up to present. The increase was initially caused by anthropogenic release of C to the atmosphere from deforestation and other land use change and management activities. Although emission from fossil fuel combustion started before industrial era, it never became dominant source of anthropogenic emissions until around 1920s to present. The average increases in the rate of fossil fuel CO_2 emission more than tripled from ~1% yr^{-1} in the 1990's to 3.7% yr^{-1} the following decade (Raupach and Canadell 2010). Several lines of evidence have confirmed that recent and continuing increase of atmospheric CO_2 concentration is caused by anthropogenic CO_2 emissions—especially fossil fuels burning: (i) atmospheric O_2 is declining at a rate comparable with fossil fuel emissions of CO_2 since combustion consumes O_2, (ii) the characteristic isotopic signatures of fossil fuels (i.e., lack of ^{14}C and depleted content of ^{13}C) is fingerprinting and leaving their mark in the atmosphere, (iii) the increase in observed CO_2 concentration has been showing regional distribution with similar patterns of increased fossil fuel burning.

3.4.1 Changes in Atmospheric Carbon Dioxide and Methane Concentrations

Since the beginning of Industrial Era in 1750, the burden of CO_2 in the atmosphere has increased by approximately 40% from 589 Pg C in 1750 to current burden of 849 ± 5 Pg C in 2015 (Ciais et al. 2013; Le Quéré et al. 2015) at an average atmospheric increase of 0.98 Pg C yr^{-1} (Le Quéré et al. 2015, 2016). The three most important sources of the anthropogenic CO_2 in the atmosphere are (i) fossil fuels (coal, oil, and natural gas) combustion, (ii) land use change—conversion of natural forests and grasslands to agriculture land, and (iii) cement production and other industrial processes. The concentration of atmospheric CO_2 is currently significantly higher than at any time during the past several hundred thousand years and steadily heading towards a GHG burden not seen for some 20 million years.

When systematic CO_2 monitoring began at Mauna Loa, Hawaii in 1958, the annual mean mole fraction was 315 ppm. The daily CO_2 average concentrations recorded at Mauna Loa station was above 400 ppm for the first time in May, 2013 (Scripps 2014). Mauna Loa station has the longest running record of direct measurements of atmospheric CO_2 concentrations (Tans and Keeling 2014). The 27% increase is mainly due to fourfold rise in anthropogenic CO_2 emissions from fossil fuel combustion and cement production. The growth has correspondingly increased from 0.7 ppm yr^{-1} in early 1960s to 2.1 ppm yr^{-1} during the last decade (WMO 2016). The annual atmospheric increase varies considerably from year to year, ranging from 0.7 ± 0.1 to 2.8 ± 0.1 ppm yr^{-1} since 1990. The natural variations in El Nino Southern Oscillation (ENSO) are the main cause of year to year variations (Bastos et al. 2013). In 2015, globally averaged CO_2 mole fraction at the Earth's surface was 400.0 ± 0.1 ppm which was an increase of 2.3 ± 0.1 ppm over the 2014 average.

Similarly, emission of CH_4, which is released during extraction and processing of fossil fuels, leaks from natural gas extraction and distribution, and biological sources including landfills, expanding rice and livestock production, has also shown similar steady increase in concentration (Prinn 2004; Ciais et al. 2014, Fig. 3.2). Levels of CH_4 reached 1845 ± 2 parts per billion (ppbv) by the end of 2015 (WMO 2016), about 2.5 times their pre-industrial value of 722 ± 25 ppb (Etheridge et al. 1996). Atmospheric CH_4 is produced by natural (40%) and anthropogenic (60%) sources.

3.4.2 Impacts of Changing Global Carbon Cycle

Atmospheric CO_2 is increasing by slightly less than half of the rate of fossil fuels emissions however, the rest of CO_2 emitted is either dissolving in the sea water and mixing into the deep ocean or is taken up by the terrestrial ecosystems through excess primary production by photosynthesis. The atmospheric CO_2 emission that is taken up by ocean and land ecosystem can be calculated from the changes in atmospheric CO_2 and O_2 content, since terrestrial processes of CO_2 exchange involve exchange of O_2, while dissolution in the ocean does not.

The CO_2 and CH_4 are the second and third most important GHGs after water vapor ($H_2O(g)$). These GHGs have strong influence on the radiative properties of the atmosphere. As a result of this increase in atmospheric CO_2 and CH_4 concentrations, the globally averaged combined land and ocean surface temperature has increased by 0.85 ± 0.21 °C over the period 1880–2014 (IPCC 2014; Jones et al. 2013; Ruedy et al. 2015). Such large increases in atmospheric CO_2 over a short time relative to historical variations and associated increase in global temperature, together with patterns of anthropogenic activity emitting CO_2 and CH_4 to the atmosphere, which will likely continue for foreseeable future, raises serious concerns about the imbalances in the C cycle and their implications.

There is a growing concern that this increase in atmospheric CO_2 and CH_4 concentrations are causing significant warming and other changes in global climate by altering the heat and water balances of Earth's surface and atmosphere (Fig. 3.3). Ample physical evidence shows that CO_2 and CH_4 are the most important climate relevant GHGs in Earth's atmosphere, since ($H_2O(g)$) condenses and precipitate from the atmosphere at the current temperatures.

A second impact of anthropogenic CO_2 emission is ocean acidification, which refers to continuous decline in pH and reduction in ocean's carbonate (CO_3^{2-}) mineral saturation state (Caldeira and Wickett 2003; Johnson and White 2014). Over the past 200 years, the oceans has taken up ~40% of the atmospheric CO_2 emissions, which has caused pH level of world's oceans to drop by 0.1 unit,

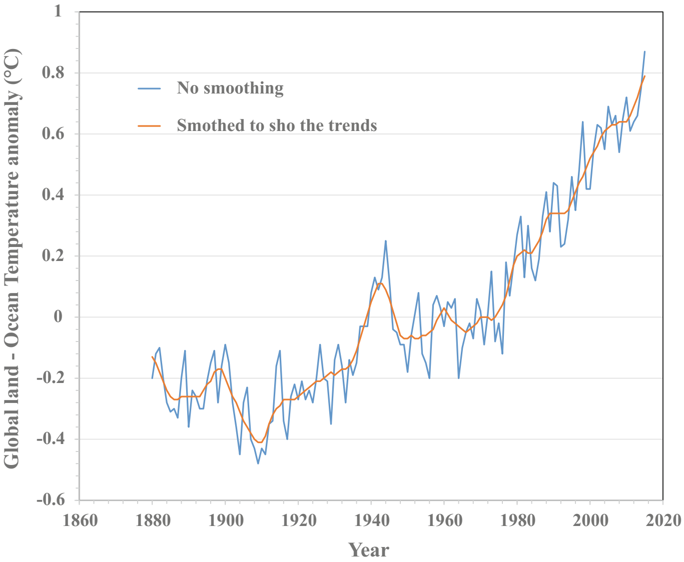

Fig. 3.3 Global land-ocean temperature anomaly. *Data source* http://data.giss.nasa.gov/gistemp

amounting to 30% increase in ocean acidity (Johnson and White 2014). Although this uptake slows the rise in atmospheric CO_2 concentration considerably, it also alters ocean chemistry with potentially negative consequences for marine life (Zeebe et al. 2008). This process has a detrimental consequences for a variety of marine organisms (Hoegh-Guldberg et al. 2007).

Other factors associated with changes in ocean chemistry include effects on speciation which could alter metal bioavailability (Millero et al. 2009), reduced NH_3/NH_4 ratios affecting ammonia oxidation rates, N cycling, and marine sources of atmospherically active trace gases (Hutchins et al. 2009; Beman et al. 2011), reduced ocean overturning (Gregory et al. 2005), sea level rise as a result of warmer temperatures and melting ice (Tyrrell 2011).

Terrestrial ecosystems are absorbing an estimated 20–30% of the annual anthropogenic CO_2 emissions, which have increased since 1990 (Le Quéré et al. 2009, 2015), probably as a response to CO_2 fertilization. Evidence suggests that the elevated atmospheric CO_2 as a result of anthropogenic CO_2 emissions is causing CO_2 fertilization effect, i.e., increase in leaf photosynthesis with rising atmospheric CO_2 concentration (Zak et al. 2011; De Kauwe et al. 2013). However, the magnitude of CO_2 fertilization and its continuity into the future are a matter of debate (Newingham et al. 2013).

Many countries have adapted a global warming temperature rise limit of 2.0 °C or below relative to pre-industrial level as a guiding principle for mitigation efforts to reduce climate change risks, impacts and damage (IPCC 2007; IPCC 2014). Despite this restriction, global emissions of CO_2 from fossil fuels combustion and cement production have continued to grow by 2.5% yr^{-1} over the past decade (Friedlingstein et al. 2014). Similarly, two thirds of the CO_2 emission quota consistent with a 2.0 °C temperature limit has already been used, and the remaining one third will likely be exhausted in the next 30 years at the emission rates of 2014 (Raupach et al. 2014; Friedlingstein et al. 2014).

Moreover, the projection of CO_2 emissions and its attendant effects of climate modification and ocean chemistry alteration have typically focused on the century time-scale, most notably until the year 2100 (IPCC 2007; IPCC 2014). However, from geological, and biogeochemical perspective, CO_2 released by anthropogenic activities have the longer term consequences which are equally, if not more important. For example, a large fraction of anthropogenic CO_2 emissions stays in the air for long time. One quarter of the anthropogenic CO_2 will remain airborne for several centuries (Archer et al. 2009; Kharecha and Hansen 2008). This implies that even if anthropogenic emission is capped at a fixed concentration, the climate change will continue for several centuries as the C cycle adjusts to new equilibrium. In contrast, if the fossil fuel combustion is fully controlled, the climate and geochemical recovery will take tens to hundreds of thousands of years well after the emissions have ceased (Archer et al. 2009), while biotic, in terms of biodiversity and ecosystem functioning may take millions of years (Alroy 2008). The complexity of the Earth system, particularly involving the contribution of physical feedbacks has made the prediction of future responses of the Earth system, and climate prediction difficult.

The accelerating CO_2 emission rate and failure of environmental sinks to keep pace with current emission rates makes stabilization of atmospheric CO_2 during this century even tougher challenge. The atmospheric CO_2 stabilization requires that net emission level off, and eventually drop to near zero, where the rate of CO_2 addition to the atmosphere equals the rate at which the natural systems can remove them (i.e., anthropogenic CO_2 emissions is balanced by the natural sink capacity). To achieve this stabilization requires transformation of energy systems worldwide, which will require many decades of development and deployment. The current GHG burden will lead to warmer future, both in our lifetime and for generations to come as energy balance of the Earth systems slowly adjusts to new equilibrium with rising GHG concentrations. Anthropogenic activities, mainly fossil fuel burning, forest clearing and agricultural activities are primarily responsible for current GHG burden. Anthropogenic CO_2 emissions are occurring on top of an active natural C cycle that circulates C between atmosphere, terrestrial biosphere and ocean reservoir on time scale ranging from days to millennia, while the circulation of geologic reservoir with other reservoirs have much longer time scales (Archer et al. 2009). There is a strong consensus that global C cycling and climate perturbations from land use change and fossil fuels CO_2 release extends hundreds of thousands of years into the future. Although the atmospheric lifetime of CO_2 is relatively short, $\sim$100 years, modeling reveals that 20–35% of CO_2 emitted to the atmosphere now will still be in the atmosphere after 2–20 millennia. Therefore, for all practical purposes fossil fuels and land use change CO_2 emissions should be considered irreversible, and any eventual stable atmospheric CO_2 will be dictated by total accumulated emissions over the preceding centuries rather than balance of emissions and removals (Allen et al. 2009; Mackey et al. 2013).

The burning of fossil fuels which transfers large masses of fossilized C from geological reservoirs of coal, oil, and natural gas from slow domain, and releases large masses of C in the form of CO_2 into the atmosphere (i.e., a fast domain reservoir), has dominated the anthropogenic CO_2 emissions in recent years. The cumulative emissions from fossil fuel combustion from 1870 to 2013 are estimated at 390 ± 20 Pg C. An additional 3 Pg C were emitted for the earlier period 1750–1869 (Le Quéré et al. 2015). The 1800s and 1900s experienced a great rise in combustion of fossil fuels—coal, petroleum, and natural gas, releasing into atmosphere large quantities of C that was originally stored in geological formation. About 45 Pg C were emitted from land use change from 1750 to 1869, of which, 10 Pg C was emitted from 1850 to 1869. From 1870 to 2013, land use change released 145 ± 50 Pg C (Houghton et al. 2012). Emission of C from fossil fuel combustion started before the Industrial Era, however, fossil fuel combustion exceeded the CO_2 emissions from burning and decomposition of dead plant material that accompanied forest clearing for agricultural land use from around 1920 (Houghton 2014) and continued to be the dominant source until present (Chap. 6). Terrestrial systems are also an anthropogenic source of CO_2 when land use change leads to loss of C from soils and plants. Deforestation and other land use changes also release C to the atmosphere, as well as reducing the vegetation uptake of CO_2 from the atmosphere. More than 75% of Earth's ice free land shows evidence of alteration as a result of human residence and land use, with less than a quarter remaining as wild lands supporting just 11% of terrestrial net primary production (Ellis and Ramankutty 2008). Although the influence of human on the fluxes and reserves of C among the three reservoirs—atmosphere, terrestrial biosphere, and ocean represent a small changes in total pools of C, but it represent a significant perturbation of a global C cycle.

The evidence of human impact on the planet is so great that it has been suggested that the Earth has entered a new geological era dominated by human activity called 'Anthropocene' (Steffen et al. 2007; Raupach and Canadell 2010), to distinguish it from the preceding Holocene which started at about 12,000 years before present (BP; i.e., 1950). However, there is no agreed definition of Anthropocene, and also no agreeable official starting date (Doughty 2013). Because climate change may be the most important global impact of human on the planet it may also be good proxy for the onset of Anthropocene. The dates most often quoted to correspond with the start of Anthropocene is the onset of Industrial Revolution when extensive burning of coal began to greatly change the composition of the atmosphere (Steffen et al. 2007). Anthropogenic influence and trends are evident in the global C cycle and its connection with climate. Other changes in Earth system stemming from human activities include biodiversity loss and disturbance of nutrients cycles.

With the invention of steam engine, the internal combustion engine and other technological advances and economic elements of Industrial Revolution, human societies discovered the great value of fossilized C formed hundreds of millions of years ago as the energy source for economic growth. The global carbon cycling through atmospheric, terrestrial, and oceanic reservoirs have dispersed the greater part of these anthropogenic emissions, locking the CO_2 into terrestrial plant biomass and soil, and also by dissolution into oceans.

3.5 Global Warming

In 1896, Arrhenius concluded that the continued emission of CO_2 from combustion of fossil fuels could lead to a warmer climate. Although his succeeding calculations were incomplete, his fundamental conclusions of linking fossil fuels combustion, the radiation balance of the Earth system, and global climate have been confirmed by both models and studies of the past climate (Chap. 8). This early pioneering discussion of the relationships between changes in atmospheric CO_2 concentration and climate change became motivation for advancing scientific studies in many fronts. The research on global C cycle has enabled scientists to attribute the rising in atmospheric CO_2 concentrations primarily from anthropogenic activities, especially the burning of fossil fuels—coal, oil, and gas, together with the changing land use, especially deforestation. During the late 1950s, a growing number of scientists became interested in studying anthropogenic effects on the global C cycle (Keeling 1958; Revelle and Suess 1957). This interest is exemplified by Revelle and Suess (1957) who pointed out that: "*The human beings are now carrying out a large geophysical experiment of a kind that could not have happened in the past nor be reproduced in the future. Within a few centuries we are returning to the atmosphere and oceans the concentrated organic carbon stored in sedimentary rocks over hundreds of millions of years. This experiment, if adequately documented, may yield a far reaching insight into the processes determining weather and climate. It therefore becomes of prime importance to attempt to determine the way in which carbon dioxide partitioned between the atmosphere, the oceans, the biosphere and the lithosphere*" (Revelle and Suess 1957) [pp. 19–20]. In this single phrase, Revelle and Suess (1957) described the connections between anthropogenic production of CO_2 and the array of earth and biological processes that cycles C over geologic time, and it has been a rallying desire to understand human manipulation of the atmospheric CO_2 as a profound global environmental change.

The basic understanding of the link between CO_2 emissions and climate change led to investment into formation of United Nations Framework Convention on Climate Change (UNFCCC) in 1992 signifying international recognition of vulnerability of global climate to human actions. The Intergovernmental Panel on Climate Change (IPCC) established by the United Nations as a tool for synthesizing scientific information has released 5 comprehensive assessments on scientific basis of climate change. Also, International Council for Science Unions (ICSU) has orchestrated several projects devoted to global C budget. The following 4 chapters are the synthesis of some current understanding on the global C cycling.

3.6 Conclusion

The overall objective of global C cycle research has been to account for complete mass balance of the CO_2 produced by anthropogenic activities—including its sources, processes that removes it from the atmosphere i.e., its sinks, and forms in which C from CO_2 is stored—i.e., reservoirs. Research directed towards improving projection of C cycle is increasingly intertwined with research directed towards improving understanding of climate change and improving climate change projection (Friedlingstein et al. 2006; Field et al. 2007). The challenge of controlling the increase in atmospheric concentration of CO_2 is the topic of expanding concern which has attracted national and international attention. The following chapters will describe the global carbon cycling with the emphasis on how the anthropogenic activities have altered this cycling.

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Chapter 4
The Global Carbon Inventory

Abstract The main reservoirs of global carbon (C) cycle are the atmosphere, the biosphere, the oceans, and the lithosphere. The atmospheric C inventory consists of almost entirely carbon dioxide (CO_2) and methane (CH_4) with the current (2015) atmospheric concentration of 400 ppm and 1845 ppb for CO_2 and CH_4, respectively. This is equivalent to atmospheric burden of nearly 849 and 3.7 Pg C for CO_2 and CH_4, respectively, compared to 589 and 1.49 Pg C in 1750 at the beginning of the Industrial Revolution. Most of the increase since the begining of Industrial Era is associated with the anthropogenic activities of fossil fuel combustion and land use change. The terrestrial biosphere contains C in living biomass of the terrestrial ecosystem and soils. The estimated C in living biomass range from 450 to 700 Pg, while soils contains an estimate of 1500–2400 Pg as soil organic C (SOC) and 720–930 Pg C as soil inorganic C (SIC) in the top 3 m depth. The terrestrial SOC is dominantly preserved in forest biomass and soils. The ocean C inventory amounts to 39,000 Pg, of which, only 700–900 Pg C exist in the surface water layer which is in direct contact with the atmosphere. More than 90% of C is present as bicarbonate (HCO_3^-). Additional 2500 Pg C is present in marine carbonate (CO_3^{2-}) sediments which are gradually transformed into sedimentary rock over the geological timescale. Of the dissolved CO_2 inventory in the ocean, 170 ± 20 Pg is of anthropogenic, with an estimated uptake of $\sim 3.0 \pm 0.5$ Pg C yr^{-1} in 2015. The distribution of C in the ocean is regulated by three processes: biological pump, solubility pump and thermocline circulation. The lithosphere, consisting of Earth crust and mantle is the largest reservoir of C. The C in Earth crust is estimated at 7.8×10^7 Pg, of which, 20% is in organic C (OC)—mostly as fossil fuels—coal, oil and natural gas. An estimated 420 ± 20 Pg C from the fossil C has been released to the atmosphere as CO_2 since the Industrial Revolution.

Keywords Carbon budget · Hydrates · Oxygen radicals · Methanotrophs · Exogenic carbon cycle · Endogenic carbon cycle

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Contents

4.1 Introduction

The global carbon (C) cycle can be divided into short-term (exogenic) cycle and long-term (endogenic) cycle. The exogenic cycle (fast C domain) consists of mainly the surface or near surface reservoirs—the atmosphere, the biosphere, the oceans and surface sediments in the oceans. The atmosphere acts as a connecting transfer station in terms of global C cycle and the other C reservoirs, such that the other reservoirs interacts with each other primarily through the atmosphere, even though the atmosphere holds only a small fraction of Earth's C. The biosphere includes terrestrial living and dead biomass, soils, continental waters, and aquatic biomass. The largest reservoir of C near the Earth's surface is the sediments. These include calcite and dolomite rocks, made predominantly of younger unconsolidated carbonate sediments on the land and ocean floor, skeletal remains of terrestrial and marine organisms, and organic matter in the sediments that consists of many different organic compounds containing reduced C (Table 4.1). During Holocene—beginning 11,700 years ago and prior to industrial era (1750) the exogenic C cycle was close to steady state as evidenced by the relatively small variations of atmospheric CO_2 recorded in ice cores, despite small anthropogenic C emissions from human induced changes in land use over the last millennia (Pongratz et al. 2009).

The endogenic cycle (slow C domain) is dominated by C in the lithosphere. The interaction between the endogenic and exogenic C cycle involves long-term release of C from Earth's crust and burial of C in sediments. The planetary average abundance of C in the whole Earth is not well constrained because C abundance in the lower mantle and core of the Earth is not well known. However, its abundance in the Earth's mantle is much lower than in the sediments, estimated as $\sim$0.008–0.015% by weight. Oxidized C is the most abundant form at the Earth's surface where it occurs as CO_2, dissolved CO_3^{2-}, HCO_3^- and carbonate in sedimentary minerals. Pure elemental C occurs in nature only in two minerals—diamond and graphite. The slow C domain interacts with the atmosphere naturally through volcanism, metamorphism and sedimentation. Over last few centuries

Table 4.1 Mass of carbon in the major environmental reservoirs

Reservoir	Carbon mass	
	Petagrams C (Pg C)	Moles of C
Atmosphere		
CO_2 (pre-industrial 280 ppm)	594	4.95×10^{16}
CH_4 (pre-industrial 722 ppb)	1.50	9.32×10^{13}
CO (current)	1.24	4.42×10^{13}
Land biota (current)		
Living biomass	700	5.83×10^{16}
Bacteria and fungi	3	2.50×10^{14}
Animals	1–2	1.25×10^{14}
Soil		
Soil organic matter	1500	1.25×10^{17}
Reactive OM		2×10^{16}
Litter and peat	250	2.08×10^{16}
Inorganic C	720	6×10^{16}
Aquatic biosphere	1–3	–
Ocean		
Dissolved inorganic carbon (DIC)	3.74×10^{4}	3.11×10^{18}
Dissolved organic carbon (DOC)	1.0×10^{4}	8.33×10^{16}
Particulate organic carbon (POC)	3	2.50×10^{15}
Marine biota	3	2.50×10^{14}
Reactive marine sediments	6.0×10^{3}	–
Sediments		
Carbonates	6.23×10^{7}	5.44×10^{21}
Organic matter	1.25×10^{7}	1.05×10^{21}
Continental crust (30 km thick)	2.58×10^{6}	2.14×10^{20}
Ocean crust (6.5 km thick)	9.2×10^{5}	7.44×10^{19}
Upper mantle (30–700 km thick)	$(8.9–16.6) \times 10^{5}$	$\sim 1.1 \times 10^{21}$

anthropogenic fossil fuels extraction and combustion, mining activities, and human induced changes in land use, erosion and river fluxes have modified slow domain interaction, however (Raymond and Cole 2003).

The global C cycle can be viewed as a series of reservoirs of C in the Earth system which is connected by exchange fluxes of C. Carbon inventories relevant to the global C cycle are atmospheric, biosphere and soils, oceans, and lithosphere. The C present in three domains of the natural environment—atmosphere, land, and water regulate the short-term global C cycle. These inventories are subject to constant fluxes as a result of web of interlinking processes. Therefore, the C in the individual reservoirs have varied considerably throughout the Earth's history. Additionally, anthropogenic activities have introduced new fluxes through various feedback mechanisms. Figure 4.1 depicts the reservoirs of C that affect atmospheric C over geologic timescales. Estimates presented for the reservoirs and fluxes among these reservoirs are from late Holocene Epoch prior to significant anthropogenic influence.

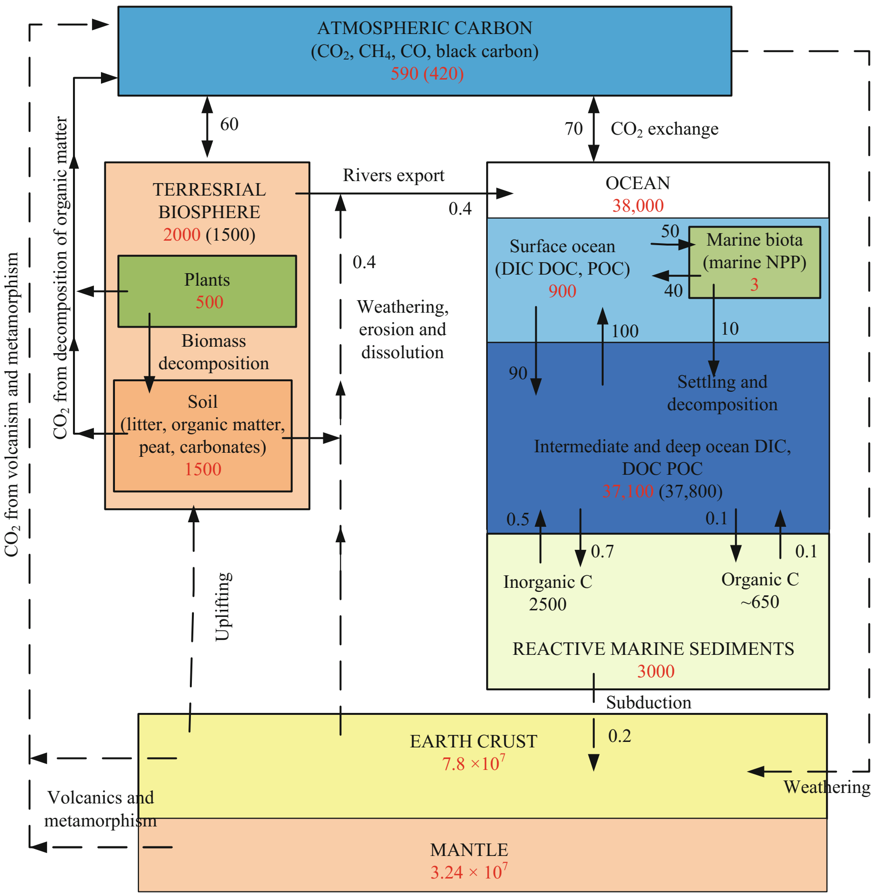

Fig. 4.1 Reservoirs (in *capital letters*, Pg C) and fluxes (*arrows*, Pg C yr^{-1}) of the pre-industrial carbon inventory. *Values in parenthesis* represent carbon inventory during glacial period and *dash lines* is the global endogenic carbon cycle. Data from Sundquist and Ackerman (2014), Sundquist et al. (2009)

4.2 Atmospheric Carbon Inventory

4.2.1 Carbon Dioxide

The C inventory in the atmosphere is dominated by CO_2 with an estimated mass of 849 Pg C in 2015 (Prather et al. 2012; Joos et al. 2013; Le Quéré et al. 2015, 2016) or ~0.04% by volume with mean residence time (MRT) in the atmosphere estimated at 5.3 years before it enters into ocean or terrestrial ecosystem. The atmospheric CO_2 concentration can be measured to within one tenth of 0.1 ppmv or 0.000001%. The average atmospheric CO_2 concentration reached 400 ppm by the end of 2015, compared to pre-industrial era concentration of 278 ± 2 ppm (atmospheric concentration of 1 ppm CO_2 is equal to atmospheric burden of nearly 2.1 Pg C). The CO_2 is completely mixed in the atmosphere in about a year, and any atmospheric gas monitoring station free from contamination will record the same year to year increase in CO_2 concentration. Because the MRT is longer than the mixing time for the atmosphere, atmospheric CO_2 shows minor regional and seasonal variations. The atmospheric CO_2 inventory prior to industrial era in 1750 is estimated at 589 Pg C (Sundquist et al. 2009; Sundquist and Ackerman 2014), indicating that the atmospheric CO_2 inventory has risen by more than 44% since preindustrial times as a result of net emissions from anthropogenic activities, including fossil fuel combustion, changes in land use and land management. During the glacial period, the atmospheric CO_2 is estimated at 420 Pg C (Sundquist and Ackerman 2014).

Atmospheric CO_2 concentration measurements were started by Charles Keeling at National Oceanic and Atmospheric Administration (NOAA) Mauna Loa Observatory, Hawaii (elevation 3400 m) in September 1957, and at South Pole the following year (Keeling et al. 1976). The atmospheric monitoring at Mauna Loa established an average value of 313.23 ppm in 1959 after full year of atmospheric CO_2 monitoring (Pales and Keeling 1965). The data also revealed increasing annual CO_2 concentration from 312.82 in 1958 to 315.83 in 1963 (Pales and Keeling 1965). The curve of continuous measurement of CO_2 concentration established over time, sometimes referred to as Keeling curve (Fig. 4.2) revealed the atmospheric CO_2 increase between 0.5 and 1 ppm yr^{-1} for the first decade of continuous measurement.

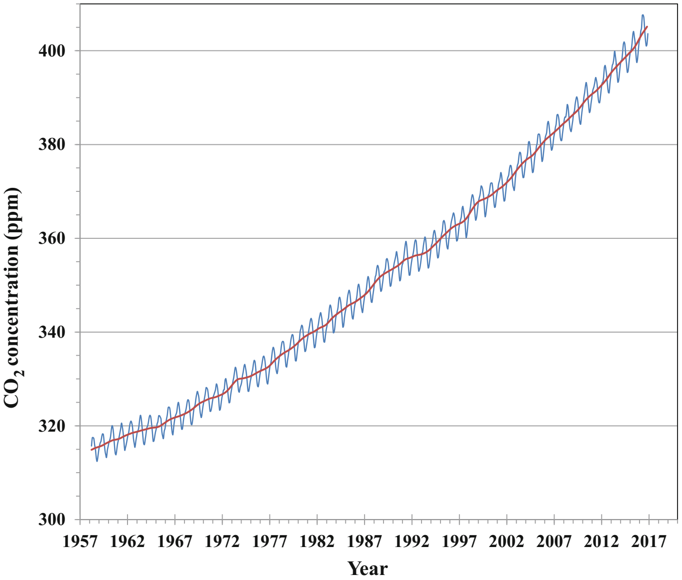

Fig. 4.2 Monthly average CO_2 concentration at Mauna Loa Observatory, Hawaii, 1958–March 2015. Data from Keeling et al. (2015)

Currently the increase is approximately 2.3 ppm yr^{-1}. The cyclical continuously rising trend is the result of CO_2 draw-down by photosynthetic production from May to September, which rebounds by almost similar amount as a result of biomass decomposition from October to April. Oscillations in the CO_2 content of the atmosphere vary in amplitude with latitude and the elevation (Bolin and Keeling 1963), and are the most pronounced in the Northern Hemisphere where major part of the continental area occurs. Smaller fluctuations of atmospheric CO_2 of the Southern Hemisphere may also be due to exchange with oceans (Keeling et al. 1984). Globally, about two thirds of terrestrial vegetation occurs in the regions with seasonal periods of growth and the remainder occurs in the moist tropics where CO_2 growth occurs throughout the year (Box 1988). This seasonal pattern of CO_2 is mirrored by atmospheric O_2 oscillations which has larger atmospheric pool and longer residence time in the atmosphere (Keeling et al. 1995, 1996). The amplitude of this annual CO_2 concentration cycle at Mauna Loa ranges from 5.7 ppm in 1960 to 6.4 ppm in 2008 (average = 6 ppm yr^{-1}) equivalent of about 13 Pg C yr^{-1} to and from atmosphere as a result of seasonal oscillations. The atmospheric CO_2 concentration is now being monitored concurrently across a large network of sampling stations distributed around the globe (http://www.esrl.noaa.gov/gmd/ccgg/trends/). The CO_2 emissions rose at a rate of 1.3% yr^{-1} during 1990–1999, but since 2000, it has been growing at the rate of 3.3% yr^{-1}, and the emissions reached 8.4 Pg yr^{-1} in 2006.

4.2.2 *Methane*

Methane (CH_4) is the second largest C inventory and the most abundant hydrocarbon in the atmosphere with current mass of ~3.7 Pg CH_4–C (Ciais et al. 2014). Pre-industrial atmospheric CH_4 burden is estimated at 1.49 Pg CH_4–C (Ciais et al. 2013; Sundquist and Ackerman 2014). The pre-industrial natural source flux strength was about 0.12–0.22 Tg CH_4–C yr^{-1} (Sundquist and Ackerman 2014), increasing to near 0.45 Pg CH_4–C yr^{-1} at the end of 20th century as a result of anthropogenic emissions (Etheridge et al. 1998; Wolff and Spahni 2007). Pre-industrial sources of CH_4 were primarily natural, while the post-industrial sources of CH_4 are both natural and anthropogenic.

Development of gas chromatography (GC) and the flame ionization detector (FID) in the 1950s enabled accurate measurements of CH_4, and led to observations of vertical CH_4 distributions in the troposphere and stratosphere and establishment of time series sampling programs in late 1970s. Systematic measurements of the atmospheric CH_4 burden led to suggestions that the concentration of CH_4 in the atmosphere was also increasing, as that of CO_2 (Dlugokencky et al. 1994). The establishment of atmospheric increase and natural the variability was confirmed by measurements from polar ice, which preserves ancient atmospheric air from which the concentration of stable trace gases can be measured. The background concentrations before 1750 was around 722 ppbv, albeit superimposed with transitions of the order of 40 ppbv during Holocene and pre-industrial period (MacFarling Meure et al. 2006; Loulergue et al. 2008b), with a slow increasing trend of the order of 5 ppbv century^{-1} (MacFarling Meure et al. 2006). The firn air measurements overlapping ice core and direct atmospheric observations reveal major increase in CH_4 during the past 200 years. The atmospheric CH_4 concentration was 880 ppbv in 1900 (MacFarling Meure et al. 2006), indicating that the majority of increase occurred in the 20th century. During the last half of 20th century CH_4 concentration were increasing by 10 ppbv yr^{-1} with shift towards isotopically heavier $^{13}CH_4$ isotopes during the 20th century (from −49 to −47‰) indicating a shift in balance of CH_4 sources towards fossil and pyrogenic CH_4 compared to light biogenic sources (Wolff and Spahni 2007). Rising concentrations of atmospheric CO_2, CH_4 and other greenhouse gases (GHGs) can alter the Earth's radiant energy balance. Recent studies have identified near linear relationship between global mean temperature and cumulative CO_2 and CH_4 emissions (Allen et al. 2009; Raupach 2013; Gillett et al. 2013). Therefore, the anthropogenic disturbance of global C cycle during the industrial era and the resulting imbalance in the Earth's C budget together with increase in atmospheric CO_2 and CH_4 have consequences for the global climate and climate change.

The CH_4 is a reduced form of C, and is much less stable than CO_2 in the atmosphere. It has an average atmospheric residence time of 5–10 years. In the environment, CH_4 is generally produced by methanogens operating in oxygen-poor environments. Natural sources include fluxes from wetlands, geological sources, termites, hydrates, and enteric fermentation in wild animals. The anthropogenic sources include rice paddies, enteric fermentation in domesticated ruminants (livestock production), coal mines, leakage from natural gas fields, landfills, and biomass burning (Prinn 2004; Ciais et al. 2014). The global budgets of CH_4 is well constrained, but the contributions of individual sources to the atmospheric CH_4 supply are uncertain by a factor of 2 or more (Cicerone and Oremland 1988). Likewise, the sizes of individual sources contributing to the atmospheric CH_4 supply are not well constrained. Additionally, the sizes of the reservoirs other than atmospheric CH_4 can only be approximated. The CH_4 hydrates comprise the largest reservoir of CH_4 in the global C cycle. The CH_4 hydrates are formed when abundant dissolved CH_4 accumulates under specific conditions of cold temperature and high pressure, the conditions commonly occurring in marine sediments below water depth of a few hundred meters in ocean, and in continental sediments at high latitudes. Changes in environmental conditions can make CH_4 hydrates unstable and yield large quantities of dissolved and gaseous CH_4. The sensitivity of CH_4 hydrates to changing environmental conditions may have played role in the past global C cycle changes.

4.2.3 Other Trace Compounds

Additional atmospheric trace gases containing C include carbon monoxide (CO) with current mass of ~0.2 Pg C (0.05–0.2 ppmv) with considerable differences between the northern and southern hemispheres, anthropogenic hydrocarbons, and black C aerosols which in total contribute a small mass ~0.05 Pg C (Ciais et al. 2014). The CO has an atmospheric residence time of only few months. Its low concentrations and short residence time is a result of its chemical reactivity with OH radicals.

Both CO_2 and CH_4 are important GHGs, along with $H_2O(g)$, nitrous oxide (N_2O) and other radiative active gases in the atmosphere, they absorb infrared radiation in the troposphere radiated from the Earth's surface that would otherwise be lost into space (Ramanathan et al. 1985; Chap. 1). The CO has no greenhouse effect, but its chemical reactivity affects the abundance of ozone (O_3) which has a greenhouse effect. Together with non-methane hydrocarbons, they modify chemical and/or radiative properties of the atmosphere.

4.2.4 Sinks

The CO_2 is removed from the atmosphere by exchange with biosphere, oceans, and lithosphere. The atmospheric CO_2 concentration is controlled by the exchange with other reservoirs. Therefore, atmospheric CO_2 is cycled naturally through other forms of C over timescales ranging from seconds to millennia and longer. Carbon from atmospheric CO_2 is converted by photosynthetic plants to plant C. Photosynthetic organisms capture sun energy and use it to convert the atmospheric CO_2 to organic compounds, a process which accounts for the presence of atmospheric O_2 which sets the redox potential for organic metabolism in terrestrial habitats.

The CH_4 plays important roles in the atmospheric chemistry and the radiative balance of the Earth. The main sink of CH_4 in the atmosphere is the oxidation in the troposphere by reactions involving hydroxyl radicals (OH^-). Some 90% of the CH_4 entering the atmosphere is oxidized through reactions initiated by the OH radical which are important in controlling the oxidation state of the atmosphere (Reeburgh 2014). Stratospheric oxidation of CH_4 provides a means of introducing water vapor above the tropopause. Its oxidation also affects atmospheric concentration of other important reactive species, including formaldehyde (CH_2O), carbon monoxide (CO), and ozone (O_3) (Wuebbles and Hayhoe 2002). The CH_4 oxidation is an important source of atmospheric CO. The concentration of CH_4 in the atmosphere reflects the balance between its oxidation in the atmosphere and its land and ocean sources. Other smaller sink include reaction processes that take place in stratosphere and troposphere through reaction with chlorine and oxygen (O_2) radicals. The CH_4 reacts with chlorine in the stratosphere to form HCl, a reservoir species for chlorine. It is estimated that about 0.03 Pg CH_4–C yr^{-1} is destroyed in the atmosphere, and 0.015–03 Tg CH_4–C yr^{-1} accumulates in the atmosphere, while the remainder is probably consumed by methanotrophs in soils (Prinn 2004) and possibly reaction with chlorine in the marine boundary layer (Allan et al. 2007). There are indications that the sinks—especially OH in the atmosphere may have changed over time

(Wolff and Spahni 2007). Atmospheric C represents only a small fraction of C in the Earth system, the rest of it is tied up in other reservoirs.

The fundamental difference in controlling mechanisms between CO_2 and CH_4 affects the dependence of responses of atmospheric CO_2 and CH_4 to abrupt perturbations. The response of CH_4 will occur relatively rapid through its rate of oxidation in atmosphere even though CH_4 has longer atmospheric lifetime, whereas the CO_2 changes will be mediated by more complex array of processes that govern its rate of exchange with other large C reservoirs. The concentration of atmospheric CO_2 increased from 278 ± 5 ppm at the beginning of industrial era in 1750, to 400 ppm in 2015 (Tans and Keeling 2014), a growth rate of over 40% with estimated annual increase of ~1.7 ppm yr^{-1} corresponding to 3.5 Pg C yr^{-1}.

The longest available ice core records from Vostok and Dome Fuji, Antarctica demonstrate that the atmospheric CO_2 and CH_4 concentrations currently are higher than the past 800,000 years (Lüthi et al. 2008; Loulergue et al. 2008a). During the Holocene ~11,700 year ago prior to Industrial Revolution, the atmospheric C inventory was close to steady state, as evidenced by relatively small variations of atmospheric CO_2 concentrations recorded in the ice cores—180–200 ppm (Petit et al. 1999; Lüthi et al. 2008).

Since the beginning of industrial era humans have been producing energy mostly by burning fossil fuels—coal, oil and gas, a process that is releasing large amounts of CO_2 and CH_4 into the atmosphere (Rotty 1983). The total fossil fuels emission from 1750 to 2015 is estimated at 410 ± 20 Pg C (Le Quéré et al. 2015, 2016). The CO_2 emissions from fossil fuels and cement production almost doubled between 1970 and 1979 decade (4.7 ± 0.2 Pg C yr^{-1}) and 2015 (9.3 ± 0.5 Pg C yr^{-1}) while that from land use change decreased from 1.3 ± 0.5 Pg C yr^{-1} to 1.0 ± 0.5 Pg yr^{-1} (Le Quéré et al. 2015, 2016).

Many of currently proposed options to mitigate climate change will require management of global C cycle and concentrations of atmospheric CO_2. The management that includes reducing anthropogenic CH_4 and CO_2 emission from sources such as fossil fuels, land management, reduction of CH_4 emissions from animal production system, and enhancing C sinks such as uptake by plants and soils (sequestration) could also provide C offsets. Successful management of Earth's C budget requires solid scientific understanding of C cycle and the ability to account for all C pools, fluxes and changes, and to distinguish the effects of human actions from the natural variability. Therefore, accurate assessments of anthropogenic CO_2 emissions and their redistribution among the atmosphere, ocean, and terrestrial biosphere is important for better understanding of global C cycling and also project future climate change.

The consequences of unbalanced C budget with C accumulating in atmosphere mostly as CO_2 and CH_4 is not fully understood, but it is generally accepted that they extend beyond climate change alone. For example, experimental studies have suggested that for many plant species, rate of photosynthesis often increases in response to elevated CO_2 concentrations, potentially increasing the plant growth and possibly agricultural crops yields in the future. This concept is generally termed as "CO_2 fertilization". There is great uncertainty whether the CO_2 fertilization will continue into the future with prolonged exposure to elevated CO_2, and whether this has potential benefit on plants when future climate change is taken into consideration, however. Other climate change feedbacks, incidence of extreme climate events, and changes in temperature and precipitation will result in changes in land and water regimes that will subsequently affect agricultural productivity.

4.3 Carbon Inventory of the Biosphere and Soils

The terrestrial biosphere reservoir contains C in living vegetation of terrestrial ecosystem estimated to range between 450 and 700 Pg C (Prentice et al. 2001), and is somewhat less than that presently in the atmosphere. Global net primary production (NPP) on the terrestrial ecosystem is estimated at 60 Pg C yr^{-1}. Considering land vegetation alone, each molecule of atmospheric CO_2 has the potential to be captured in in net primary production in about 13.7 years. Soil organic carbon (SOC) pool is estimated at 1500–2400 Pg C in the top 3 m (Jobbagy and Jackson 2000). About 1500–1600 Pg C is contained in the top 1 m depth (Batjes 1996), while SOC content in the second and the third meter depths is estimated at 490 and 350 Pg C, respectively (Jobbagy and Jackson 2000). Reserves of inorganic C stored in soils (SIC) are estimated at 720–930 (Schlesinger 1982; Sombroek et al. 1993). The SIC occurs largely as carbonate minerals—such as calcite ($CaCO_3$) and dolomite ($(CaMgCO_3)_2$). This inventory has declined by approximately 10% since pre-Industrial Era, and mostly from 19th century as a result of land use changes and land management practices such as deforestation, conversion of grasslands to agricultural land use, and intensive agricultural practices. The SOC inventory to 1 m soil depth can be further classified based on MRT within the soil into labile C ranging from plant and animal detritus which has residence time <10 years, estimated at 350 Pg C, intermediate C with residence time of 10–1000 years, estimated at 1100 Pg C and almost inert or recalcitrant C which is inaccessible to biological decomposition processes, and remain in soil until physically removed by water or airborne transport, with residence time >1000 years estimated at 150 Pg C. Microbial biomass C can account for 0.3–5% of the SOC or 13.9–26 Pg C, and soil microbial biomass and its activity are highly dependent on the presence of available C substrates and moisture availability. The mean turnover time for the microbial biomass C is 0.13–0.24 year in the humid tropics and 1.4–2.5 years in soils of temperate regions (Wardle 1992; Serna-Chavez et al. 2013).

Most of the terrestrial C is stored in vegetation and soils of the world's forests. Forests covers ~30% of the land surface and is estimated to hold ~75% of living organic C. Global forests store 240–500 Pg C (average 300 Pg C) in living biomass, equivalent to 140 ppm of CO_2 in the atmosphere (Mackey et al. 2013). About half of world forests have been cleared, and the rate of forest clearing is estimated at $0.16 \times 10^6\ km^2\ yr^{-1}$ (FAO 2010). The remaining world forest is estimated at $40 \times 10^6\ km^2$, of which, $\sim 14.4 \times 10^6\ km^2$ or 36% is the primary forest (FAO 2010). In addition to deforestation, forests have been degraded by land use activities such as logging and soil disturbances that deplete forest SOC pools and stocks and emit CO_2. However, CO_2 emissions from global forest land degradation are poorly quantified. Together with soils, forests hold about 50% of world's C in the terrestrial ecosystem (Houghton 2004). The C in living biomass and soils of the major terrestrial biomes are presented in Table 4.2.

Terrestrial ecosystems play an important role in the global C cycle, both as repository of C inventory, and as a source and sink for the closely balanced CO_2 fluxes. Terrestrial plants fix C in the form of CO_2 known at the ecosystem level as gross primary production (GPP) through photosynthesis estimated at 123 ± 8 Pg C yr^{-1} (Beer et al. 2010). Tropical forests assimilate 34% of the global GPP and have the highest GPP per unit area, while savannah account for 26%, the second most important biome. Terrestrial GPP is the largest global C flux, which drives ecosystem functions of respiration and growth, and contributes to food, fiber and wood production for human and animals' welfare. The GPP and respiration also controls land-atmosphere CO_2 exchange and provide the capacity of terrestrial ecosystem to partly offset anthropogenic CO_2 emissions.

Carbon fixed into plants is recycled through plant tissues, litter, and soil carbon and can be emitted back into atmosphere through autotrophic plant respiration, heterotrophic microbial and animal respiration, and other disturbance processes

Table 4.2 Estimates of global terrestrial carbon pools and net primary production aggregated by biomes

Biome	Area (10^9 ha)	Carbon pools (Pg C)			Net primary production (Pg C yr^{-1})
		Plant	Soil	Total	
Tropical forests	1.745 ± 0.5	276 ± 64	214.5 ± 1.5	490.5 ± 62.5	17.8 ± 4.1
Temperate forests	1.01	99 ± 40	126.5 ± 26.5	225.5 ± 66.5	7.3 ± 0.8
Boreal forests	1.37	72.5 ± 15.5	404.5 ± 66.5	477 ± 82	2.9 ± 0.3
Tropical savannahs and grasslands	2.505 ± 0.255	72.5 ± 6.5	255.5 ± 8.5	328 ± 2	16.3 ± 1.4
Temperate grasslands and shrub lands	1.515 ± 0.265	16 ± 7	235.5 ± 59.5	251.5 ± 52.5	6.15 ± 0.85
Desert and semi deserts	3.66 ± 0.89	9 ± 1	175 ± 16	184 ± 15	2.45 ± 1.05
Tundra	0.755 ± 0.195	4 ± 2	118 ± 3	122 ± 5	0.75 ± 0.25
Croplands	1.475 ± 0.125	3.5 ± 0.5	146.5 ± 18.5	150 ± 19	5.45 ± 1.35
Wetlands	0.35	15	225	240	4.3
Total	15.025 ± 0.095	560 ± 94	1789 ± 222	2349 ± 128	61.25 ± 1.6

Adopted from Prentice et al. (2001)

Table 4.3 Soil carbon inventory component and lifetimes

Component	Inventory	Residence time (years)
Plant and animal detritus	350	<10
Modified soil carbon	1100	10–1000
Inert carbon	150	>1000
Total inventory	1600	

such as fires on a very wide range of timescales ranging from seconds to millennia (Table 4.3). About half ($\sim$60 Pg C yr^{-1}) of GPP is reemitted through plant autotrophic respiration, and the remainder ($\sim$60 Pg C yr^{-1}) is retained as net primary productivity (NPP), resulting in biomass growth. Because CO_2 uptake by photosynthesis occurs only during the growing season, whereas CO_2 release by respiration occurs nearly all year round, the greater vegetated land mass in the northern hemisphere imparts characteristic seasonal growth and decay cycle of land plants in atmospheric CO_2 concentration observed in Fig. 4.1 (Keeling 1960).

Soil respiration, primarily from microbial communities that feed on plant detritus and root exudates (i.e. heterotrophic respiration) returns a further $\sim$55 Pg C yr^{-1} to the atmosphere. Under the steady state, the remaining balance is made up by the emissions back to the atmosphere as a result of natural fires and dissolved organic C export by rain water runoff into the rivers, making net terrestrial ecosystem production approximately zero. A significant quantity of terrestrial C $\sim$1.7 Pg yr^{-1} is transported from soils to rivers headstreams. A fraction of this is outgassed as CO_2 by rivers, lakes and coastal waters to the atmosphere, a fraction is buried in freshwater organic sediments, and the remaining ($\sim$0.9 Pg yr^{-1} is delivered by river channels to the coastal oceans as dissolved inorganic, organic, and also particulate organic C (Tranvik et al. 2009). However, anthropogenic activities during industrial era have disturbed the steady state, and therefore, the estimated uptake of C from the atmosphere into terrestrial ecosystems is currently estimated at 2.8 Pg C yr^{-1}. Terrestrial biosphere inventory contains C in organic compounds both in vegetation biomass and dead organic matter in soils.

Changes in terrestrial C inventory and related fluxes as a result of human activity have also been a major contributor of the atmospheric CO_2 concentration increase during industrial times. An estimated 190 ± 65 Pg C have been emitted to the atmosphere due to land use changes since the beginning of industrial era, but most of the emissions occurred after 1850 (Houghton et al. 2012; Le Quéré et al. 2015, 2016). This indicates a potential for the terrestrial ecosystems to have a significant impact in mitigating increases in atmospheric CO_2 concentrations. Losses of soil C due to land use result from accelerated decomposition and soil erosion.

4.4 Carbon Inventory of the Oceans

The ocean holds 50 times more C content than the atmosphere and 70 times more than world's terrestrial vegetation. The current oceanic C inventory amounts to ~39,000 Pg C. The large C content of the ocean results from C chemistry. When CO_2 dissolves in ocean it reacts with water and carbonate (CO_3^{-2}) to form bicarbonates (HCO_3^-) according to the equilibrium reaction (Eq. 4.1):

$$CO_2 + H_2O + CO_3^{2-} \leftrightarrow 2HCO_3^- \tag{4.1}$$

The sum of HCO_3^{2-}, CO_3^{2-} and CO_2 forms dissolved inorganic C (DIC) which is tightly coupled via ocean chemistry. An increase in the dissolved CO_2 concentration reduces the carbonate ion concentration due to the reaction that forms bicarbonate ions. Table 4.3 shows the distribution of ocean C inventory into major forms of C. The distributions of DIC among HCO_3^-, CO_3^{2-}, and CO_2 (pCO_2) are 91, 8 and 1%, respectively (Le Quéré and Metzl 2004; Raven et al. 2005), and only CO_2 can exchange with the atmosphere. As a result, CO_2 behaves differently from other gases in the ocean, since most gases are less soluble in water and exist predominantly in the atmosphere. For example ~1% of global O_2 is in the ocean, while ~99% exists in the atmosphere. However, 98.5% of the C in the ocean—atmosphere systems is in the ocean, but most of it is in DIC form. The chemical equilibrium among the three forms of DIC—HCO_3^-, CO_3^{2-} and CO_2 is responsible for the high solubility of CO_2 in the oceans, and also sets up a buffer for changes in ocean C. The chemical buffering of CO_2 in sea water is quantified by buffer factor (ε) also known as Revelle factor (McNeil and Sasse 2016). The ε varies with temperature, but globally averaged as ~10, and is defined in Eq. 4.2:

$$\varepsilon = \frac{\frac{\Delta pCO_2}{pCO_2}}{\frac{\Delta \sum CO_2}{\sum CO_2}} \tag{4.2}$$

where, pCO_2 is the partial pressure of CO_2 (i.e., the atmospheric CO_2 concentration at equilibrium with that of sea water), $\sum CO_2$ is total inorganic C (i.e., DIC), Δ refers to change in the variable. Equation 4.2 indicates that pCO_2 is sensitive to small changes in DIC. The lower the ε, the larger the buffer capacity of seawater and ε increases with pCO_2, a positive feedback. The variability of ε in the ocean depends mainly on changes in pCO_2 and the ratio of DIC to total alkalinity. The present value of ε ranges from 8 to 13 (Sabine et al. 2004) with a global average of ~10, which indicates that a change in pCO_2 is approximately 10 times the change in the total CO_2. The significance of this is that the storage capacity of the ocean for the excess atmospheric CO_2 is 10 times lower than it might be expected by comparing reservoir sizes, and the ocean will become increasingly resistant to taking up CO_2 as the buffer factor increases.

Most of the C in the ocean is retained in the intermediate and deep waters, and only 700–1000 Pg C exist in the surface layers of ocean, the part that is in direct contact with the atmosphere (Fig. 4.1). In addition, ocean contains a pool of dissolved organic C (DOC, ~700 Pg C) of which, substantial fraction has a turnover time of 1000 years or longer (Hansell et al. 2009). About 6000 Pg C is in reactive ocean sediments (Sundquist 1986). But the turnover of C in the sediments is slow, and is generally not considered as part of active or short-term global C cycling, even though it plays an important role in determining long-term CO_2 concentration in ocean and atmosphere. About 2500 Pg C in marine C sediments is gradually transformed into sedimentary rocks over geologic timescale. Under certain conditions, C buried in marine sediments may not be recycled back to the atmosphere and oceans for millions of years. These deposits comprise the limestone and organic rock formations.

The marine biota, predominantly phytoplankton and other microorganisms represent a small organic C pool (~3.0 Pg C) which is turned over very rapidly in days to few weeks. Plankton growth is limited by the availability of light, nutrients and also by grazing. Nutrients are abundant in the intermediate and deep ocean but are depleted over most of the ocean surface where growth occurs. The Southern, Northern, and Equatorial Pacific oceans have high nutrients in surface waters but lower biological productivity due to low availability of iron (Fe) needed for chlorophyll synthesis by plankton (Bakker et al. 2005; de Baar et al. 2005). The oceanic plants are microscopic, with high productivity, but production does not accumulate, since most of it is grazed or decomposed in the surface waters. Only fraction (~25%) sinks into the deeper ocean. Marine plants are the base of the oceanic food chain which eventually returns respired CO_2 to the ocean surface and atmosphere. Only small fraction (~0.2 Pg C yr^{-1}) of SOC exported by biological processes as both soft tissues and carbonate pumps from the surface reaches the sea floor where it can be stored in sediments for millennia and longer (Denman et al. 2007). The distribution between living and dead form of OC in ocean is very different compared to that of land. The ratio of C in living and dead biomass is 1:3 on the land and 1:300 in the ocean. The mass of animal life in the ocean is nearly the same as that on the land, but with different trophic structures in the two environments.

It is estimated that ~155 ± 31 Pg C in 2010 or 16% of the oceanic inventory is of anthropogenic origin, with an estimated uptake of one third of anthropogenic C over the industrial period (Khatiwala et al. 2013). However, there are indications that the oceanic C uptake has changed during the past few decades (Le Quéré et al. 2015, 2016). The ocean and land sink rate between 1959 and 2012 declined by about one third (Raupach et al. 2014), implying that CO_2 sinks increased more slowly than the excess CO_2.

In relation to CO_2 chemistry outlined above, the distribution of C in the ocean is driven by three key processes which keep the atmospheric CO_2 lower than it should be: (i) the solubility pump, (ii) the biological pump, and (iii) marine carbonate pump or the thermocline circulation. The CO_2 is more soluble in cold than in warm water, and when water becomes warmer, CO_2 is outgassed to the atmosphere. The CO_2 is approximately 2 times more soluble in cold mid-depth and deeper depth waters than the surface waters around the Equator. It is well established that at large scale, the oceans take up CO_2 mostly in the temperate and high latitudes. The solubility effect creates higher CO_2 uptake at mid- and high latitudes in Arctic and Antarctica, where currents transport warm waters from low latitudes around the Equator. The oceans outgas CO_2 generally in the tropical waters, and the air-sea CO_2 flux distribution is controlled by CO_2 solubility and by biological and physical processes.

The solubility effects create higher CO_2 uptake at high and mid-latitudes, and the currents transport warmer surface waters from low latitudes. The warming process occurs mostly in equatorial regions, where upwelling brings cold water from the deep ocean into contact with the atmosphere. Most of the intermediate and deep waters of the ocean were last in contact with the atmosphere at cold temperatures of high latitudes, and the CO_2 at the depth has equilibrated with the atmosphere at high latitudes and colder surface temperatures, which creates concentration of C up to 5% higher at depth than at the surface which keeps the atmospheric CO_2 lower than the average concentration of surface waters (Murnane et al. 1999), this process is described as solubility pump. This process has ramifications in that as the global temperature increases, the sea uptake of anthropogenic CO_2 decreases, resulting into larger fraction of CO_2 remaining in the atmosphere.

The biological pump involves photosynthetic uptake of CO_2 by marine biota, mostly plankton; which take up DIC and nutrients from marine surface waters. When the marine biota dies or excretes detritus, the dead tissues can either remain in water as dissolved organic C (DOC) and transported by water currents, or aggregate into particulate organic C (POC) and sink while entraining C as it falls. Sinking DOC and POC creates a flux of C from surface to deep-ocean where it is isolated from atmosphere for decades to centuries. The one-way flux of OC from surface waters to deep waters is termed as export production. Deep waters rich in OC are transported back to the surface by physical processes of water currents and mixing. The POC and DIC are re-mineralized by living organisms and ultraviolet degradation. However, some DOC and POC are buried into sea sediments. The entire cycle of OC consisting of export production, balanced by physical transport is what is known as biological pump. About 70% of CO_2 taken up by plankton is recycled near surface through re-mineralization back to DIC by living organisms and ultraviolet degradation. The remaining 30% sinks into the deeper waters before being converted back into CO_2 by marine bacteria (Falkowski et al. 1998), and transported large distances by currents to upwelling regions where water regains contact with the atmosphere. The net effect of sinking C is to enrich deeper waters relative to surface waters and reduce the atmospheric CO_2 concentrations. Ocean models that simulate C chemistry and ocean circulation indicate that the atmospheric CO_2 concentration would have been 720 ppmv if the two pumps—solubility and biological pump were turned off (Sarmiento 1993). The overall effect of biological and carbonate pump is to increase the concentration of C at deeper depth by $\sim 10\%$ compared to the surface ocean (Murnane et al. 1999).

Some of plankton species grow shells of $CaCO_3$ which alter the chemistry of surface waters. These shells can sink to deep ocean, causing decrease in CO_3^{2-}

concentration, and drive the equilibrium in Eq. 4.1 to the left and release CO_2, and thus having opposite effect of biological pump. This process is called carbonate pump or biological counter-pump. Thus, the marine carbonate pump operates to counter the marine biological soft tissue pump with respect to its effect on CO_2. Two bicarbonate ions split into one carbonate and one dissolved CO_2 molecules which increases partial pressure in the surface waters and drive the release of CO_2 to the atmosphere. The three processes—solubility pump, biological pump, and carbonate pump drive the distribution of C between organic and inorganic fractions and its transport in the ocean, and eventual deposition in sediments.

The C needed for photosynthesis in the ocean is supplied from atmosphere in dissolved form by exchange with air at the ocean surface. It is estimated that 70 Pg C yr^{-1} was exchanged between surface waters and the atmosphere before industrial revolution. This rate has increased to ~90 Pg C yr^{-1} as a result of anthropogenic activities in the post-industrial revolution. Atmospheric CO_2 is exchanged with the surface ocean through gas exchange. This exchange flux is driven by the partial pressure difference between the air and the sea, and is controlled by global circulation, which exchanges surface and deep water on 500–1000-year timescale, the geochemistry of surface waters particularly the removal of carbonate ions by ionic reactions and by precipitation.

In addition to CO_2 uptake, oceans influence climate by storing and transporting large amounts of excess energy and fresh water, and by exchanging these properties and also C with the atmosphere. About 93% of the excess heat energy stored by the Earth over the last 50 years is found in the upper 2000 m of the ocean (Church et al. 2011; Levitus et al. 2012) due to large mass and heat capacity of sea water relative to air, and circulation which connects the surface and the interior ocean. The rest of heat goes to melting sea and land ice, warming the land surface, and warming and moistening the atmosphere (Trenberth et al. 2014). Global integrals of 0–700 m depth show a gain in heat content from 1971 to 2010 (Levitus et al. 2012). The estimated heat gain for the 40-year period ranges from 82 to 154 TW (Levitus et al. 2012). This resulted in the warming rate of 0.09–0.13 °C $decade^{-1}$ in the upper 75 m, decreasing to about 0.015 °C $decade^{-1}$ by 700 m. As a result of the warming of the ocean water, the dissolved O_2 in the ocean thermocline has generally decreased since 1960, howbeit with strong regional variation (Keeling et al. 2010; Helm et al. 2011). The interaction of ocean and atmosphere and cryosphere is considered to control the climate variability and change on timescales from seasons to millennia.

The inorganic C chemistry dynamics that describes the ultimate uptake capacity of oceans is well understood. However, the capacity of oceans for uptake of CO_2 also depends on circulation dynamics and biological processes associated with them. The rise in CO_2 concentration has resulted in an increased rate of uptake of CO_2 by the oceans reducing the atmospheric C inventory by an estimated 2.6 ± 0.5 Pg C yr^{-1}, roughly a quarter of the anthropogenic emissions estimated at 10.3 ± 0.5 Pg C yr^{-1} for the period from 2006 to 2015 (Le Quéré et al. 2015, 2016). The additional uptake of anthropogenic CO_2 by the oceans has resulted in an increase in surface ocean acidity, as the carbonate buffer has been depleted in these waters. The fast ocean uptake of anthropogenic CO_2 from the atmosphere has caused a shift in marine carbonate system, decrease the CO_3^{2-} ions concentration, and lower ocean water pH. Even though the mean pH of the surface waters of open ocean remains mildly basic with the pH range of 7.8–8.4 (Feely et al. 2009), since the start of industrial era, pH of the surface ocean waters has decreased by 0.1 units, which corresponds to a 30% increase in H^+ ions and decrease in annual mean CO_3^{2-} by 10% (Feely et al. 2004, 2009; Sabine et al. 2004; Orr et al. 2005) with the largest reductions in North Atlantic and smallest reduction in the south tropical Pacific. The regional variations in the size of pH decrease are consistent with stronger buffering capacities of the sub-tropical gyres compared to Polar regions (Egleston et al. 2010). Ocean acidification is a major threat to marine organisms at all trophic levels and may substantially alter marine ecosystem functions (Fabry et al. 2008) as well as biogeochemical processes and other aspects. The ocean acidification chemistry is straightforward. As anthropogenic CO_2 enters the sea water, it combines with water to form carbonic acid (H_2CO_3), which in turn dissociates to form HCO_3^- and CO_3^{2-} releasing proton (H^+ ions) to the surrounding water (Eq. 4.1). Ocean acidification will limit the ability of the ocean to increase CO_2 uptake in response to future increases in atmospheric CO_2 concentration. The ocean provides slow acting buffer to stabilize atmospheric CO_2 concentration, and any atmospheric perturbation will be dissipated by absorption into the ocean over a timescale of centuries. Other potential consequences of ocean acidification include impacts on coral and other marine organisms that build their skeleton shells from $CaCO_3$. Experimental evidence suggest that ocean acidification will dramatically reduce the distribution of warm water corals which precipitate easily dissolved $CaCO_3$. Ocean acidification and climate change are the two leading reasons to care about the changing C cycle and the accumulation of anthropogenic CO_2 in the atmosphere (Orr et al. 2005).

4.5 Carbon Inventory of the Lithosphere

The lithosphere consisting of Earth's crust and mantle represent the geological C source and sink. The C accounts for only 0.27% of the elements in the Earth's crust (Kempe 1979), and yet it is the basis of life on Earth. The Earth crust is estimated to hold 7.8×10^7 Pg C in sedimentary rocks (Table 4.1; Sundquist et al. 2009; Sundquist and Ackerman 2014), of which, 20% is in the form of organic C and the remainder as limestone. Fossil fuels—coal, oil and gas together accounts for 9833 ± 1100 Pg C (Fig. 4.3; Sundquist and Ackerman 2014; Sabine et al. 2004) or 0.05% of the total organic C present in sedimentary rocks. Fossil fuels became the primary energy source in the Industrial Era, and predominantly after 1900. Fossil fuels are the product of pre-historically stored residual organic C, especially those from 354 to 290 million years ago originally a constituent of the atmosphere of a younger earth in the Carboniferous Age when atmosphere contained ~1500 ppm CO_2 concentrations when the evolution of Earth's first primitive forest began the slow process of biogeological sequestration which retained the

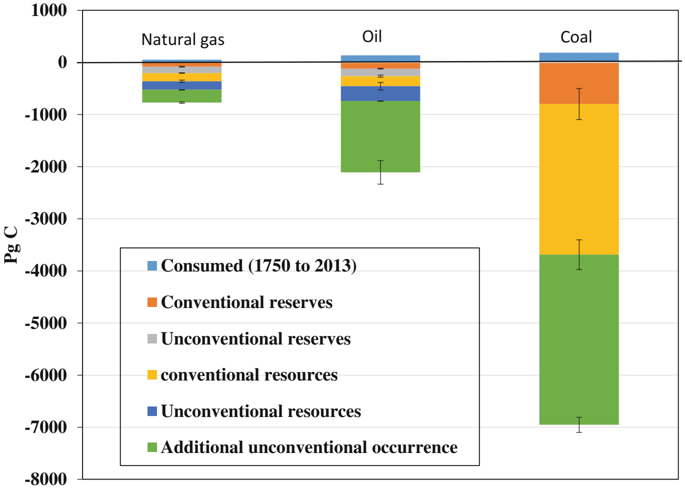

Fig. 4.3 Global fossil C energy reserves and resources. Conventional reserves are the identified economical deposits which can be recovered by using current technology, while the resources are the occurrences of economic interest which are recoverable through unconventional technology. Additional unconventional resources are believed to be unrecoverable. *Data sources* Sundquist and Ackerman (2014), BP (2015), Moomaw et al. (2011)

organic C relatively unoxidized. During this time, luxuriant plant growth and geological activity combined to bury a fraction of each year's biomass growth. The organic materials of plants that escaped oxidation, became buried in Earth, and over time were transformed into fossil form through diagenesis processes. The energy stored in chemical bonds of fossil fuels is released during combustion. Over a period millions of years, this gradual burial led to the accumulation of vast pools of fossil fuel. The burial of C also led to doubling of atmospheric oxygen (O_2) from ~10% by volume ~205 million years ago to current concentration of 21% (Falkowski et al. 2005; Falkowski and Isozaki 2008). Increased rock weathering also occurred as a result of higher atmospheric O_2 concentrations (Table 4.4).

Since the dawn of Industrial Age in 1750, and particularly after the invention of internal combustion engine to present the global use of fossil fuels—oil, natural gas and coal has dominated the energy supply and replaced the traditional use of plant biomass. During this period, an estimated 420 ± 20 Pg C has been released to the atmosphere in the form of CO_2 by anthropogenic use of fossil energy. This rapid rise in fossil fuel use produced a corresponding rapid increase in atmospheric CO_2 concentration (Fig. 4.1). The amount of C in fossil fuel reserves and resources conventional and unconventional oil and natural gas as well as abundant coal not yet burned has the potential to add large quantities of CO_2 to the atmosphere over the coming decades (Fig. 4.3). The amount of C stored in recoverable fossil fuels is larger than any other C reserve in reactive pool except the deep ocean, and is about 10 times more than the atmospheric C. Until about 150 years ago, this reserve of C was not a significant part of the short-term global C cycling. The industrial

Table 4.4 Ocean carbon inventory

Component	Inventory (Pg C)
Bicarbonate	38,000
Carbonate ions	1300
Dissolved CO_2	740
Dissolved organic carbon	<700
Marine biomass	<10
Total	39,000

revolution and the resultant increase in demand for reliable energy sources changed that. Since the beginning of industrial era fossil fuel extraction from geological reservoirs and their combustion has resulted in transfer of significant amount of fossil C from slow domain into the fast domain causing an unprecedented, major human induced perturbation in the global C cycle. However, over the geologic time scales, natural changes in the balance of fluxes in the global geological C cycle have caused past variations in atmosphere CO_2 concentrations, which have been associated with past changes in climate (Chap. 5).

The C inventories are subject to constant flux as a result of a various interlinking natural processes. In addition, anthropogenic activities have introduced new fluxes, and the effect of these has modified some of the natural fluxes through various feed mechanisms. It is estimated that about 45% of anthropogenic CO_2 emissions remains in the atmosphere. The genesis of Earth's ozone layer is closely bound with the emergence and development of photosynthesis, the conversion of atmospheric CO_2 into organic matter by plants, and a process known as carbon fixation and driven by the energy provided by sunlight. Photosynthesis is accompanied by the emission of O_2 which can be converted into ozone O_3, a process occurring mainly in the stratosphere and driven energetically by ultraviolet (UV) radiation from the Sun. Through its capacity to absorb the damaging UV radiation, the ozone layer vastly increased the capacity of life forms to colonize the land and upper layer of the hydrosphere. Photosynthetic production of O_2 has increased the atmospheric concentration of O_2 from merely trace to its current concentration of 21%. This permitted development of relatively complex and warm blooded animals such as mammals which need large amount of energy to maintain their body processes; with insufficient atmospheric O_2 the energy generation by the metabolic conversion of food would have been inadequate. On the other hand, the over-oxygenated atmosphere could result into frequent biomass fire. As fire converts biomass C to CO_2, however, O_2 levels would be lowered once more.

Current atmospheric levels of O_2 and CO_2 are the two aspects of our environment that have been shaped by the biogeochemical cycles. The remarkable long-term stability of Earth's surface temperature and decrease in ultraviolet irradiation of the biosphere were noted several decades ago by James Lovelock and were instrumental in development of his "Gaia theory", which suggests that the planet is essentially a 'super organism' characterized by homeostasis: the tendency for organism to maintain a fairly constant internal environment as in the case of temperature control in the human body, which is likewise regulated by means of negative feedback (Lovelock and Margulis 1974). Example of such feedback is the increased photosynthesis with rising atmospheric levels of CO_2 with the attendant effect of increase in C fixation and O_2 production.

However, there are also cases of positive feedback that tend to accelerate processes of environmental change. All these remaining equal, a rise in atmospheric CO_2 levels will be mirrored in a temperature rise, promoting microbial respiration of C present in soils in turn for example, leading to elevated soil emissions of CO_2 from arable soils (Ogle et al. 2005). Other examples of positive feedback are encountered in the context of ice ages of the past 3 million years. These ice ages were triggered by Milankovitch cycles associated with peculiarities of Earth's movement around the Sun (Jansen et al. 2007).

Life on earth depends on cycling of C through various transformations and transfers among atmosphere, oceans, soils, plants, rocks, and sediments. The C cycle encompasses many cycling processes, including the daily cycle of plant growth, decay, and geologic cycle of sediment burial and weathering. These processes are linked to exchange of CO_2 with the atmosphere. The atmospheric CO_2 is cycled naturally through other forms of C overtime scales ranging from seconds to millennia and longer.

4.6 Conclusions

The global C cycle can be viewed as series of reservoirs and C in the earth system which are connected by exchange fluxes of C. Two domains of global C cycle can be distinguished (i) the fast domain with large exchange fluxes and relatively rapid reservoir turnover which consists of C in the atmosphere, the ocean surface, ocean sediments and on land in vegetation, soils and freshwaters. The reservoirs turnover times (i.e., mass of C divided by exchange flux) range from a few years for the atmosphere to decades to millennia for the major C reservoirs of land, vegetation and soil and the various domains in the ocean (ii) slow domain consisting of huge C stores in rock and sediments, which exchanges C with fast domain through volcanic emissions of CO_2 chemical weathering, erosion and sediment formation. Turnover times of the geological reservoir or the slow domain is millions of years. Natural exchange fluxes between the slow and fast domains of C cycle is relatively small (<0.3 Pg C yr^{-1}) and can be assumed constant in short timescales. Carbon is removed from the atmosphere by photosynthesis, cycled through plant tissues, litter and soil C and then released back into the atmosphere by autotrophic and heterotrophic respiration and some disturbance processes such as fires on a very wide range of tissue from seconds to millennia. Ocean contains significantly large pool of C estimated at 39,000 Pg C. Most of ocean C is retained in deep waters. The lithosphere is the largest reservoir of C, estimated at 7.8×10^7 Pg C, some of it is fossil fuel reserves. The global coal, oil and natural gas resources remaining are estimated at 6954, 2010, and 770 Pg C, respectively. Fossil fuel C reserve is the product of biological and geological processes that have occurred over hundreds of millions of years.

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Chapter 5
Historical Perspectives of the Global Carbon Cycle

Abstract Quantifying atmospheric carbon dioxide (CO_2) concentration and carbon (C) cycling during Earth's ancient greenhouse episodes is essential for accurately interpreting current global climate and predicting the future climate due to elevated CO_2 concentrations associated with increased anthropogenic CO_2 concentration. While the trends in atmospheric CO_2 concentration and global C cycling in recent decades are clear, its significance is only revealed when viewed in the context of geological timescales. Beyond the direct instrumental record, air bubbles trapped in ice cores has provided concentrations of greenhouse gases (GHGs) and reveal that the atmospheric CO_2 concentration was 278 ± 2 ppmv at the onset of the Industrial Revolution in 1750. Ice core covering a period of the past 800,000 years, which incorporates the past eight glacial/interglacial cycles have been extracted and characterized. During the glacial/interglacial period, the atmospheric CO_2 concentration oscillated between 170 and 200 ppmv during glacial periods and 240–290 ppmv during interglacial periods, revealing coupling of the global temperature and atmospheric CO_2 concentration. It is broadly accepted that changes in atmospheric CO_2 concentration constitutes a feedback rather than the primary cause of climate variation observed during the glacial-interglacial cycles, however. The drivers and mechanisms controlling the onset of and variations in atmospheric CO_2 concentration during glacial/interglacial are highly debated, but it is broadly accepted that the succession of glacial/interglacial cycles are driven by the shape of Earth's orbit and tilt of its spin axis termed as Milankovitch cycles. However, the exact mechanisms on how these cycles initiate or terminate glacial cycle is still not known. The C cycling processes and the associated changes in climatic factor acts as feedback mechanisms. During the interval of global warming from the last glacial maximum to early Holocene, climate system underwent large-scale changes, including decay of ice sheets which caused the sea level rise, estimated at 80–120 m and net release of CO_2 to the atmosphere, which increased the atmospheric concentration to 265 ppmv at early Holocene. An increase of 20 ppm is observed during Holocene, which is generally attributed to decomposition of deep-sea organic matter (OM). The C cycling and atmospheric CO_2 concentration for geologic timescale beyond the ice core record is normally reconstructed from geological proxies and geochemical models. On a multimillion-year timescale the

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long-term or geochemical C cycle involves slow exchange of C between the rocks (i.e., lithosphere) and the surface reservoirs consisting of the atmosphere, the ocean, the biota and soils. The processes affecting the atmospheric CO_2 concentration are the uptake of atmospheric CO_2 during silicate minerals, transport, precipitation and burial of carbonates as limestone as well as burial of organic matter (OM), thereby removing CO_2 from the atmosphere. Degassing of CO_2 from rocks and buried OM on the other hand return CO_2 back to the atmosphere. Geologic records show evidence of coupling of climate and C cycling during Phanerozoic. The atmospheric CO_2 concentration was low (<500 ppm) during the periods of long-lived cooler continental temperatures, and widespread glaciation may have occurred during these times. In contrast, during warmer periods, the CO_2 concentration was high (>1000 ppm). These records, are highly correlated with the atmospheric CO_2 predicted from geochemical models.

Keywords Quaternary · Phanerozoic · Cenozoic · Precambrian · Change in carbon cycle · Holocene · Abrupt climate change

Contents

5.1 Introduction

The cycling of carbon (C) is essential to the maintenance of life, to climate, and to the chemistry and composition of the atmosphere and oceans. Increasing concerns about the future trajectory of its atmospheric carbon dioxide (CO_2) and global temperature as a result of the changing global C cycle in response to anthropogenic emissions of CO_2 and methane (CH_4) has made the understanding of current global C cycle a matter of societal urgency because of concerns about the effects of anthropogenic activities on atmospheric and ocean chemistry and the associated global climate. The emerging theme from the research on global C cycle and its influence on climate is that the current and future events cannot be isolated from geologic history of the global C cycling. Therefore, understanding of present abrupt changes in global C cycle and its implications for current and future global climate change can be improved by examining the relationship between past natural variability of the global C cycling and the past abrupt climate change events preserved in the geological records. Such knowledge of Earth's past can provide context for future climate change. The atmospheric CO_2 concentration currently is at 400 parts per million by volume (ppmv), and continuing on business as usual path of fossil fuel energy use will raise it to ~900–1100 ppmv by the end of this century (IPCC 2014), the concentration which has not been observed in reconstruction for the past ~30–50 million years.

Paleo data preserved in geological record provide information on Earth system response to atmospheric composition and external forcing, and also the understanding of Earth system feedbacks on timescales longer than few centuries, which are not possible to be evaluated from existing short instrumental records. Therefore, quantifying atmospheric CO_2 of the ancient atmosphere provides a firm basis for assessing the linkage between atmospheric CO_2 concentrations, the biosphere and the ocean chemistry that is required for the understanding of geologic past and prediction of future, most notably its effects on global temperature through its greenhouse effect. The Earth system mechanisms that were responsible for past variations in atmospheric CO_2 and CH_4 concentrations are likely to operate in the future as well. Therefore, past archives of C and climate dynamics is useful for providing knowledge and possibly constraints for biogeochemical models applied to the future projections. Atmospheric CO_2 concentration affects many other aspects of the biosphere including productivity, distribution of terrestrial vegetation, exchange of energy and water vapor between the land and the ocean surface through its role on greenhouse effect. Numerous methods for evaluating the past atmospheric CO_2 concentration have been developed and refined over the past two decades. The most reliable method has been the determination of the composition of atmospheric air trapped in glacial ice (Friedli et al. 1986; Petit et al. 1999; Siegenthaler et al. 2005; Lüthi et al. 2008). However, this method is only useful for the past 800,000 years (Augustin et al. 2004; Siegenthaler et al. 2005; Lüthi et al. 2008) because of the absence of ice older than this period. Thus, other geological proxies and geochemical modeling have been applied to determine older geologic records.

This chapter describes the current knowledge of the global C cycle prior to the anthropogenic influence. The processes and events that extend back through geologic time with special emphasis on natural exchange of C between the Earth's surface reservoirs—the atmosphere, the oceans, the biosphere and reactive sediments and also between surface reservoirs and the deep reservoirs in the lithosphere—the Earth's crust and the mantle are described. The overall relationship between the global C cycle and its influence on the global climate is the main focus of this and the subsequent chapters. The main objective is to utilize information about the past variations in the global C cycle archived in geological proxies to understand the modern environmental changes and prediction of changes based on the historical events. The C cycling and climate system are tightly coupled in the Earth system at both short and long timescales (Willeit et al. 2014). For example, the atmospheric concentration of CO_2 which directly influences the Earth's temperature through its effect on radiative balance depends on the rate of C uptake by the land and oceans, which are also dependent on climate. The atmospheric CO_2 influences climate through its effect on radiative balance of the Earth and climate in turn affects CO_2 through its control on the organic matter (OM) decomposition and the ocean circulation. The effect of climate on land and ocean C cycle can be represented in terms of surface temperature dependence, since many C cycle processes are affected either directly or indirectly by changes in temperature (Friedlingstein et al. 2003). Geological proxies indicate that temperature and CO_2 co-varied in the past on timescales ranging from glacial/interglacial cycles to El Nino Southern Oscillation (ENSO) variability, and the existing data indicate that high temperatures are highly correlated with high atmospheric CO_2 concentrations (Scheffer et al. 2006; Lüthi et al. 2008).

The objective of global carbon cycle and climate studies is to understand the contemporary climate change based on the studies of atmospheric chemistry from a global network of monitoring stations as well as from firn and ice cores sampled from polar-regions and other geological proxies inferred from rock records extending beyond the available ice core sampling to Precambrian. Natural variability of the historical global C cycle and the related climate change, including the abrupt changes beyond the instrumental observation can be gained from reconstructing a range of past environmental conditions determined from geological proxies in combination with numerical models, and this information can be used to predict the future C cycling and climate change. The quantitative understanding of the level of atmospheric chemistry during the geologic past helps in predicting the future response of high atmospheric CO_2 concentration to global climate, since the Earth system mechanisms which were responsible for the past variations in atmospheric CO_2 concentration will probably operate similarly in the future. In this context, construction of precise and continuous paleo atmospheric CO_2 records is essential for providing the understanding of the global C cycle. Through the study of the geological history of global C cycling, three themes which have emerged are: (i) different processes control C cycling over different timescales, (ii) relatively abrupt changes have played central role in the evolution of C cycle throughout the Earth's history, and (iii) geologic C cycling over all timescales pass through the atmosphere and the hydrosphere, and this course unites the entire C cycle and allows even its most remote constituents to influence global environment and biosphere (Des Marais 2001).

Throughout the Earth's history, the principal forms of C in the atmosphere have been CO_2 and CH_4, and it is these primary C-containing trace gases through which C cycling over all timescales has played crucial and distinct roles in influencing the Earth's surface environment and in the development of life. The CO_2 represents aerobic, while CH_4 represents anaerobic form of C cycling. The CO_2 is the medium of photosynthesis, metabolism, and OM decomposition. Its transformation in weathering and carbonate (CO_3^{2-}) precipitation supplies a major portion of Earth's sedimentary rocks and volatiles while contributing to C cycling through the lithosphere. The CH_4 is released from OM trapped in rocks and sediment and anaerobic microbial metabolism (Chap. 7). It can also be released from marine hydrates (also termed as clathrates) in the ocean. The CH_4 is believed to have played more important roles of altering global C cycling in geological past and is more sensitive indicator of changes in Earth's processes than CO_2, although the major transfers of large masses of C in the global C cycle are generally associated with cycling of CO_2. Together, CO_2 and CH_4 are the primary C compounds through which C cycling has influenced the Earth's surface.

5.2 Mechanisms of Geologic Carbon Cycling

5.2.1 Timescales of Carbon Cycling

In studying the factors that contributes to C cycle change over the geological timescale (i.e., millions of years), the relative importance of various reservoirs (Chap. 4) and processes depends on timescales under consideration. Therefore, it is important to distinguish the relative importance of various processes and C reservoirs that affect global C cycle over timescales under consideration. Two main timescales of C cycling defined by fundamentally different modes of C cycling are short-term or biological C cycling and geological C cycling.

5.2.1.1 The Short-Term Carbon Cycling

Over relatively short timescales (1–1000 years), the common variations in atmospheric C involve the exchange of C with the terrestrial biosphere (i.e., vegetation and soils) and the oceans (Fig. 5.1). The short-term C cycling is what is normally thought of as the 'C cycle' or biological C cycle, and it involves the natural processes that transfer, redistribute, and exchange of C among the Earth's surficial reservoirs—the atmosphere, the biosphere, and the ocean. The fluxes to and from these reservoirs define the modes of the C cycle change in short timescales. Detailed discussion of this C cycling is covered in Chaps. 6 and 7. As the short-term C cycling proceeds, the concentrations of the atmospheric CO_2 and CH_4, the two principal forms of C in the atmosphere, can change as a result of perturbation of the C cycle. Since they are greenhouse gases (GHGs), changes in their concentrations can involve climate change (i.e., global warming or cooling) over centuries and

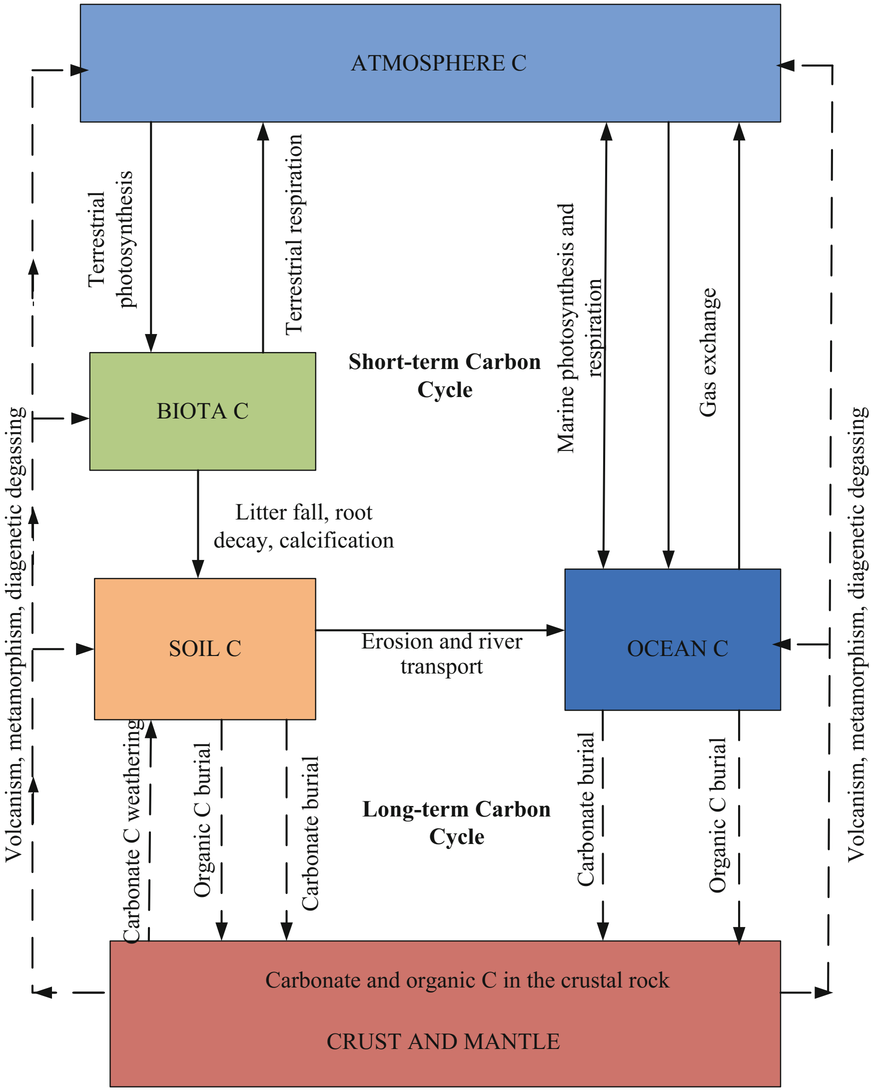

Fig. 5.1 A simplified short-term and long-term carbon cycles. *Boxes* represent carbon reservoirs while *line* and *arrows* represent carbon flux flows between the reservoirs. *Dash lines* represent C flux to and from long-term geologic reservoir. Adopted with modification from Berner (1999, 2004)

millennial timescales. For the intermediate timescales of 1000–<1,000,000 years, reactive C in the upper layers of marine sediments also contributes to atmospheric C variations. The exchange of C through CO_3^{2-} dissolution/precipitation and O_2

diagenesis controls the fluxes of the reactive ocean sediments. Although the fluxes are small, they are significant enough to affect the ocean-atmosphere chemistry at the intermediate and long timescales.

5.2.1.2 The Long-Term Geologic Carbon Cycling

Back further in geologic time (i.e., multimillion-year timescale), the exchange of C between rocks and combined atmosphere-biosphere-hydrosphere-soil system must be taken into account. For these timescales a completely different C cycling dominates. This is the long-term or geochemical C cycle (Fig. 5.1). Many C cycle trends observed in the geologic time cannot be explained by the transfer, exchange and redistribution of C among the Earth's surface reservoirs—atmosphere, biosphere and oceans alone. In these timescales, the exchange of C between crustal rocks and combined atmosphere-biosphere-atmosphere-soil system gives rise to the geochemical or long-term C cycle, which have the dominant influence on atmospheric CO_2 and also O_2 (Berner and Caldeira 1997). The three C cycling modes operate simultaneously, and distinguishing their effects is the most challenging problems in understanding the geologic evidence of C cycle change.

Mechanisms of Long-Term Geologic Carbon Cycle Change

Although C undergoes constant cycling at all the timescales, and the short-time C cycle likely causes some degree of variability in intermediate and long-term, the geologic record reveals more substantial changes that requires the influence of imbalances in exchange between Earth's surficial C reservoirs and the rocks of the Earth's crust (Sundquist and Ackerman 2014). Geochemical or long-term C cycling involves exchange of C between deep buried sediment rocks and underlying mantle on the one hand and the surficial reservoir consisting of combined atmosphere, oceans, biosphere, and soils on the other (Berner and Caldeira 1997). Thus, CO_2 is transferred from the atmosphere to CO_3^{2-} rocks through weathering and sediment burial. The burial of OM in both marine and non-marine sediments also removes CO_2 fixed by photosynthesis from the atmosphere-biosphere cycle. The atmospheric CO_2 concentration and consequently the atmospheric greenhouse effect on a multimillion-year timescale is affected by geochemical C cycling (Berner and Caldeira 1997; Berner 2004). The processes that distinguish geochemical cycle of C from the short-term C cycle also exert dominant influence on the atmospheric O_2 concentration over these timescales.

The amount of C in the Earth's crust, estimated at 7.56×10^7 Pg C (Berner et al. 1983; Berner 2004) vastly exceeds the amount of C stored in the atmosphere, biosphere, and ocean combined (4.3×10^4 Pg C, Table 5.1). The atmosphere could not have stored too much CO_2 because greenhouse warming effect would have become excessive in the past and higher life would have perished. In addition, oceans cannot store large amounts of dissolved C because accumulation of high

Table 5.1 Masses of carbon in various reservoirs

Reservoir	Carbon mass (Pg of C)
Carbonates in rocks	6×10^7
Organic carbon in rocks	1.5×10^7
Ocean HCO_3^- + CO_3^{2-}	4.2×10^4
Soil carbon	4×10^3
Atmospheric CO_2	0.8×10^3
Biosphere C	0.6×10^3

concentration of HCO_3^- in the ocean would lead to super saturation and triggering the removal of carbonates by precipitation. Therefore, appreciable quantities of C cannot be stored in surficial reservoirs because the biosphere is limited in size by the sink capacity of land and ocean (Berner and Caldeira 1997). A persistent imbalance in the exchange of crust C could, in principle, cause a drastic depletion or buildup of C at the Earth's surface that cannot be attained through short-term C cycling. In order to maintain a close balance between atmospheric CO_2 inputs and outputs, it is necessary that some restorative mechanism be operative. As a result, a rise in atmospheric CO_2 put into play a counteractive process that will work against the CO_2 increase in geologic timescale. The commonly accepted process which provides negative feedback, which also exhibit an explicit functional dependence on atmospheric CO_2 is the response of silicate weathering to changes in climate (Berner et al. 1983). High global temperatures and the associated greater rainfall on continents caused by higher CO_2 concentration results into enhanced CO_2 removal through faster silicate weathering at a multimillion years timescale.

Processes of Long-Term Carbon Cycling

The principal processes of geochemical C cycle are: (a) the uptake of CO_2 from the atmosphere and its transformation during the weathering of Ca and Mg silicate and carbonate minerals to dissolved bicarbonate (HCO_3^-), which is then transferred to the oceans by rivers and precipitated as $CaCO_3$ and $MgCO_3$ minerals (Berner et al. 1983; Berner and Kothavala 2001), (b) the weathering of ancient OM on the continents and the burial of new OM in marine sediments, (c) the thermal breakdown of carbonate minerals and OM at deeper depth through metamorphism, diagenesis, and magmatism with the transfer of the resulting CO_2 or organically derived reduced gases which become oxidized to CO_2 by O_2 back to the Earth's surface (Fig. 5.1).

Partitioning of CO_2 between various surface reservoirs and between surface and endogenic reservoirs is the main determinant of CO_2 concentration in the atmosphere over the geological timescale. The study of gradual geologic C cycle involves seeking the potential causes of change and the feedback mechanisms that might limit the extent of change (Berner and Caldeira 1997). The feedback mechanisms have been identified in the balances between CO_3^{2-} weathering and sedimentation, silicate weathering and metamorphic decarbonation, organic C production and oxidation. Therefore, long-term changes in atmospheric CO_2 concentrations is driven by changes in tectonic processes—such as volcanic and metamorphic degassing, silicate weathering drawdown, and sediment burial (Berner et al. 1983; Ruddiman 1997). Vascular plants may accelerate silicate weathering and also create a new sink for the atmospheric CO_2 through the formation and burial of recalcitrant OM in marine and non-marine sediments (Crowley and Berner 2001).

Although the fluxes of CO_2 via degassing and silicate weathering along with OM weathering and burial is small at a short timescale of 1–1000 years, when it is integrated over millions of years, these fluxes are very large compared to the mass of C in the surficial reservoir systems. Since 1750, humans have perturbed the geochemical C cycle by burning of fossil fuels—the organic C (OC) extracted from sedimentary rocks that would have otherwise oxidize slowly by weathering, and also deforestation of natural vegetation, resulting into increase in atmospheric CO_2 and CH_4 concentrations which have not been observed over the past 2 million years (M yrs) (Ridgwell and Zeebe 2005). For example, it is estimated that the maximum change in atmospheric CO_2 that could be attained by burning all terrestrial biomass and equilibrating the resulting CO_2 with the ocean would be less than 25% increase in atmospheric CO_2 concentration from those of the current concentrations (Berner 1989). In contrast, changes in long-term C cycle have likely resulted in past increases in atmospheric CO_2 concentrations more than 10 times the current concentrations, resulting in an intense global warming (Crowley and Berner 2001), as is discussed later in this chapter.

The Silicate-Carbonate Weathering-Decarbonation Cycle

Over millions of years, CO_2 is removed from the atmosphere through weathering by silicate minerals and through burial in marine sediments of C fixed by marine plants (Berner 1998). The terrestrial vegetation has enhanced the rate of silicate weathering which consumes CO_2 and releases base cations that end up in the ocean. This long-term geochemical C cycle transfers C between rocks and surficial reservoirs consisting of the ocean, the atmosphere, the biosphere and soils.

The most abundant anion delivered by the rivers to the oceans as a result of silicate weathering is bicarbonate (HCO_3^-), and most of the HCO_3^- in rivers comes from weathering of CO_3^{2-} rocks, i.e., limestone and dolomite. A representative generalized weathering dissolution of silicate by CO_2 reaction equation for Ca is (Eq. 5.1):

$$2CO_2 + 2H_2O + CaSiCO_3 \rightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4 \qquad (5.1)$$

The dissolved Ca^{2+} and HCO_3^- are carried by groundwater to rivers and by rivers to the ocean where they are precipitated through sedimentation or by reef and planktonic organisms (biological process) as $CaCO_3$ in sediments and H_4SiO_4 to silica (Eqs. 5.2 and 5.3):

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \tag{5.2}$$

$$H_4SiO_4 \rightarrow SiO_2 + 2H_2O \tag{5.3}$$

Net reaction for weathering and sedimentation for Ca and Mg (Eqs. 5.1–5.3):

$$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2 \tag{5.4a}$$

$$CO_2 + MgSiO_3 \rightarrow MgCO_3 + SiO_2 \tag{5.4b}$$

Equation 5.4 is one of the key reaction of the long-term C cycle, and represents the transfer of C from the atmosphere to the rock by means of weathering and marine CO_3^{2-} sedimentation. Similar reactions occur for Mg, Mg–Ca, and CO_3^{2-}. However, weathering of Mg-silicates does not necessitate the formation of Mg-containing carbonates. The dissolved Mg from weathering delivered to the ocean undergoes a series of different reactions with basalts that results in liberation of Ca^{2+} that is precipitated as $CaCO_3$ (Berner 2004). In this way, CO_2 is removed from the atmosphere and buried as limestone. If reactions in Eq. 5.4 were to continue alone together with the resupply of CO_2 from the ocean, all atmospheric CO_2 would be exhausted in about 300,000 years (Sundquist 1991).

Over millions of years, CO_2 lost to the silicate weathering and precipitation is restored by degassing of CO_2 to the atmosphere and oceans as a result of thermal breakdown of CO_3^{2-} at deeper depth by volcanism, metamorphism, or deep diagenesis, which completes the silicate-carbonate cycling, and can be represented for Ca as (Eq. 5.5), which is the reverse of Eq. 5.4:

$$CaCO_3 + SiO_2 \rightarrow CO_2 + CaSiO_3 \tag{5.5}$$

Equations 5.1–5.5 are the oversimplification of wide variety of contributing minerals and reactions however, but they can be used to illustrate the important aspects of silicate-carbonate weathering-decarbonation cycle.

In reality, silicate weathering consumes CO_2 and yields cations and HCO_3^- anions that are delivered by rivers to the ocean. The most abundant anions delivered by rivers to the oceans are HCO_3^-. Weathering involves Ca and Mg aluminosilicate such as plagioclase with Al precipitated as clay minerals. Clay minerals are then involved in reactions with Ca or dolomite to form igneous and metamorphic silicates. However, the overall principle of CO_2 uptake and release remains the same as represented in Eqs. 5.1–5.5. The rate of CO_2 removal via silicate weathering and CO_3^{2-} deposition together with excess of OC burial must equal the rate of CO_2 degassing over geological timescales. This equality is maintained by the negative feedback between CO_2 concentration, global temperature, and silicate weathering rates.

5.2.2 *The Carbonate Weathering-Sedimentation*

The most abundant anion delivered by rivers to the ocean is HCO_3^{2-}, and most of the bicarbonate alkalinity in rivers comes from carbonate rocks weathering (Meybeck 1987). However, the weathering of carbonates (Eq. 5.6) have little direct effects on atmospheric CO_2 over millions of years timescale, since no net change in atmospheric CO_2 as a result of the weathering of $CaCO_3$ followed by transport of Ca^{2+} and HCO_3^- to the ocean and precipitation of new $CaCO_3$ or $CaMg(CO_3)_2$ (Eqs. 5.6 and 5.7):

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \tag{5.6}$$

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \tag{5.7}$$

The precipitation of $CaCO_3$ (Eq. 5.7) is essentially the reverse of Eq. 5.6. The relative contribution of $CaCO_3$ (dolomite) to more recent CO_3^{2-} sediments is significantly less and comprise only <10% of modern sediments (Holland and Zimmerman 2000). Therefore, the relative contribution of recent carbonate sediments is significantly less, and precipitation of dolomite is not significant today and does not appear to have an impact on long-term atmospheric CO_2 trends. Hence, it is generally ignored in the geological C cycling (Sundquist and Ackerman 2014).

5.2.3 *The Organic Carbon Production-Consumption Oxidation Cycle*

Oxygenic photosynthesis and anaerobic respiration are the dominant reactions in the cycling of organic C (OC) and have the dominant reactions in cycling of OC since Precambrian (Des Marais et al. 1992). The production of OM by photosynthesis can be represented by the production of glucose which is the part of short-term C cycle (Eq. 5.8):

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \tag{5.8}$$

The transformation of glucose and other carbohydrates into the vast array of compounds that are buried and further transformed in sediments is beyond the scope of this chapter and will not be discussed here. Equation 5.8 in long-term C cycle represents net photosynthesis (i.e., photosynthesis minus respiration) resulting into burial of OM into sediments and is a principal process of atmospheric O_2 production that accompanies the production of OC over timescale of millions of years (Des Marais et al. 1992). Therefore, through the linkage of O_2 cycling, the long-term cycling of C is also connected to biogeochemical cycles of other elements including sulfur (S), phosphorus (P), nitrogen (N), iron (Fe) and other elements that are sensitive to oxidation state of the environment (Petsch and Berner 1998). Details of C cycling and O_2 linkage, and the connection to the biogeochemical cycles of other elements is beyond the scope of this chapter, however. The aerobic cycling of OC is completed by oxidation of OC, which is the reverse of Eq. 5.8, and it can be represented as (Eq. 5.9):

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{5.9}$$

Equations 5.8 and 5.9 demonstrate that the cycling of OC is inherently associated with the cycling of O_2. Therefore, the net production of OC relative to its oxidation is accompanied by net production of O_2. Conversely, a net excess oxidation of OC is also accompanied by the net consumption of O_2. The net burial of OC has been associated with the production of atmospheric O_2 over millions of years timescale (Shackleton 1987; Kump et al. 1991; Des Marais et al. 1992).

A special example of Eq. 5.9 is the burning of fossil fuels by humans. Coal and oil are concentrated forms of sedimentary OC which under normal processes oxidizes slowly through weathering and thermal degassing of hydrocarbons. However, humans have extracted these OC sources from the long-term geologic reservoirs at a quicker pace from geological perspective, such that oxidation of the C occurs at a rate of about 100 times faster than what would have occurred naturally. As a result, the long-term C cycle impinges on short-term C cycle, which has led to an extremely fast rise in atmospheric CO_2 (IPCC 2014).

Equation 5.9 represents georespiration—the oxidation of OC in rocks which occurs either by oxidative weathering of OM in shale and other sedimentary rocks uplifted into continents or by microbial or thermal decomposition of OM to reduced C containing gases followed by oxidation of reduced gases upon emission to the atmosphere (e.g., Eqs. 5.10 and 5.11):

$$2CH_2O \rightarrow CO_2 + CH_4 \tag{5.10}$$

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O \tag{5.11}$$

Equations 5.10 and 5.11 indicates that the modern cycling of CH_4 can be viewed as a sub-cycle of the C cycling. Under anaerobic conditions, microbial consumption of CH_4 may occur through sulfate (Eq. 5.12), illustrating important connection between C cycling and sulfur:

$$CH_4 + 3SO_4^{2-} \rightarrow HCO_3^{2-} + 3HS^- + 3H_2O \tag{5.12}$$

The sulfide produced in Eq. 5.12 is often precipitated and buried in marine sediments as iron sulfide (pyrite) (Berner 1982). The burial of both reduced forms of C and S allows O_2 to be accumulated in the atmosphere (Berner 2001), suggesting that the anaerobic consumption of CH_4 may have played an important role in geologic history of atmospheric O_2.

5.3 Geologic Carbon Cycling Evidence from Geological Proxy Data

The atmospheric CO_2 concentration over geologic time can be estimated by reconstruction from theoretical models and then attempt to devise rate laws and rates for processes involved in C cycle and how these rates may have changed over time (Royer et al. 2001a). Because the mass of C exchange between rocks and surficial reservoirs over millions of years through volcanism, weathering and metamorphism is much larger than that present in surface reservoirs, it allows the assumption that the sum of fluxes from the rocks to the surface reservoir is equal to sum of fluxes back to the rocks over millions of years (i.e., quasi steady state). This assumption therefore, enables the calculation of the atmospheric CO_2 concentration (pCO_2) over geologic timescale. However, most of existing geochemical models are unable to resolve short-term CO_2 excursions. In addition, error estimates based on sensitivity analysis tends to be too high for any meaningful long-term C cycle predictions (Royer et al. 2001a). Other limitations include simplistic assumptions, therefore ignoring other factors affecting pCO_2 such as seafloor basalt weathering, mid-plate plume degassing, and the global degassing which may not scale linearly as the modeling assumption.

As the alternatives to geochemical modeling, atmospheric CO_2 concentration during geologic times can be reconstructed from geological proxies. A proxy is a geologic record that is interpreted using physical and biophysical principles to represent some variations associated with climate variables/variations back in time. However, the data on atmospheric CO_2 concentration obtained from proxies becomes much more uncertain compared to those preserved in ice cores. Proxy measurements quantify changes in chemical, physical, and biological parameters that reflect the past changes in environment where the proxy carrier grew or existed. Many organisms alter their growth and/or population dynamics in response to changing climate, and response to these climate-induced quantities are recorded in the past growth of living and/or dead fossil specimens or assemblages of organisms —including tree rings, ocean and lake plankton, pollens, and biogeochemical properties such as stable isotopes composition and the element ratios. Proxy science is one of the emerging interdisciplinary techniques useful for constraining the evolution of atmospheric GHG concentrations in the Earth's atmosphere.

A range of geologic proxies are used to provide indirect information on atmospheric CO_2 concentration beyond direct measurements of atmospheric concentration and ice core gas composition over the last 800,000 years. They include: (i) C isotopic compositions of paleosol CO_3^{2-} nodules and pedogenic CO_3^{2-} of both the terrestrial and marine environments (Cerling 1992; Ekart et al. 1999; Retallack 2009b), (ii) the stable C isotope composition of alkenones, a plankton biomarkers (Pagani et al. 1999a, b, 2010, 2011; Seki et al. 2010; Bijl et al. 2010; Palmer et al. 2010), (iii) stomatal density and stomatal indices of fossil leaves preserved in geological features and sediments (Vanderburgh et al. 1993; Royer 2001; Kuerschner et al. 2008; Retallack 2009a), (iv) boron isotopic compositions of shallow dwelling foraminifera in marine environments (Sanyal et al. 1995; Pearson et al. 2009; Hönisch et al. 2009; Bartoli et al. 2011; Foster et al. 2012), and (v) Boron: Calcium (B: Ca) and Mg: Ca ratios in marine carbonate shells (Tripati et al. 2009). Table 5.2 summarizes the assumptions, scientific rationale, and limitation of five most advanced proxy methods.

The C isotope ratios of pedogenic CO_3^{2-} nodules (i.e., authigenic CO_3^{2-}) infer atmospheric CO_2 concentrations from calculations based on model of the steady-state diffusive mixing of soil respired CO_2 in the soil profile (Ekart et al. 1999). The CO_3^{2-} ion in soil is mostly formed biologically from respired CO_2 such as root respiration and OM decomposition and atmospheric CO_2. The rate of CO_3^{2-} weathering or groundwater CO_2 movement (pedogenic CO_2) is 100–1000 times slower than the rate of soil respiration (Cerling 1999). Therefore, it has no significant influence on CO_3^{2-} formation in soils. Because the respired CO_2 and atmospheric CO_2 components differ in their isotopic composition, the atmospheric CO_2 concentration can be estimated by assuming the knowledge of biologically derived CO_2 concentration in the soil, the $\delta^{13}CO_2$ of atmosphere and biological $\delta^{13}CO_2$. The atmospheric CO_2 can then be calculated by using the equations and mathematical models (Royer et al. 2001a). However, the dependence of soil CO_2 diffusion on temperature and moisture, the contribution of C_3 versus C_4 plants to respired CO_2, and the arbitrary choice of values for the mole fraction of respired CO_2 at different depths in the soil increases the uncertainty in this approach.

The stable C isotope composition of marine and terrestrial plant residues uses the sensitivity of $\delta^{13}C$ of atmospheric CO_2 fractionation during photosynthesis to estimate the atmospheric CO_2 concentration from fossil marine and terrestrial plant residues (Pagani et al. 1999a, b, 2010). Most phytoplankton exerts little or no active control on CO_2 entering their cells. As a result, the C isotopic composition of its biomass is a function of the C source, C assimilation pathway, and biosynthesis and metabolism of the assimilated OC and can, therefore, be used as a CO_2 proxy. As a result, the equilibrium and kinetic isotopic effects associated with photosynthesis fractionate strongly against ^{13}C. This relationship is often applied to geologic past to estimate the paleo-atmospheric CO_2 (Pagani et al. 1999a, b). The uncertainty in this method for the marine plants include variations in the dissolved CO_2 concentration of the ocean surface waters, effects of temperature, salinity, cell size, and growth rate; and for the terrestrial plants, variations in canopy CO_2 concentrations, and effect of temperature and leaf-to-air vapor pressure.

Stomatal indices of fossil leaves use the relationship between stomatal density and ambient CO_2 concentration to calculate the pCO_2, since the stomatal density of many modern plants is inversely related to ambient CO_2 concentrations (Beerling and Royer 2002). This relationship has been applied to analysis of stomatal densities of fossil plant leaves. The precision of pCO_2 estimated by this proxy is the highest of any of current proxies. This approach has proven subtle for Holocene CO_2 trends but its application to larger range of CO_2 variations and plant species remains uncertain.

The ratios of boron isotopes (^{11}B and ^{10}B) is known to depend on ambient pH in the B incorporated in the carbonate shells of marine foraminifers (Sanyal et al. 1995).

Table 5.2 Commonly used atmospheric carbon proxy methods, their assumptions, and limitations

Method	Assumptions	Scientific rationale	Limitations
Carbon isotopes in soil carbonate and organic matter: estimated applicability—0–150 million years	• Isotopic composition of soil CO_2 is reflected in soil CO_3^{2-} below a depth of 50 cm • The concentration of respired CO_2 is known • Isotopic composition of atmospheric CO_2 is known or can be inferred • Soil CO_3^{2-} were precipitated in the vadose zone in exchange with atmospheric CO_2 • The original depth profile of a paleosol can be determined • Burial diagenetic effects are minimal or can be quantified	Atmospheric pCO_2 affects the relationship between the $\delta^{13}C$ of soil CO_2 and the $\delta^{13}C$ of soil organic matter at depth in certain soil types, and measure of these isotopic parameters can be used to calculate past pCO_2	• Method works better for some soils than the others • CO_2 loss is difficult to quantify • Effects of late diagenesis may be difficult to quantify
Alkenone (plankton biomarker) carbon isotope: estimated applicability—0–100 million years	• Measured alkenone C isotope is accurate and precise • Ambient aqueous partial pressure of CO_2 has quantifiable relationship with plankton that can be distinguished from nutrient-related physiological factors such as algal growth rate cell size and light limited growth • Aqueous pCO_2 is in equilibrium with atmospheric pCO_2 • The C isotope fractionation in modern alkenone-producing species is the same as in ancient species and constant through time • Levels of biological productivity can be calculated • The C isotope ratio of aqueous CO_2 in mixed layer can be determined • Sea surface temperature can be determined • Atmospheric pO_2 is known or assumed • Diagenetic effects are minimal, or can be quantified	Measurement of C isotope ratios of marine sedimentary alkenones or other organic compounds allows determination of the of the isotopic fractionation factor during C fixation from which pCO_2 can be calculated	• Alkenones are often rare or sometimes absent in oligotrophic areas • Method relies on empirical calibration and $\delta^{13}C$ is sensitive to other nutrient related variables and other environmental factors • Method has only been used successfully to reconstruct glacial-interglacial changes
Stomata in plant leaves: estimated applicability—0–400 million years	• Measured stomatal index is accurate and precise • Measured stomatal index is representative of the plant	The relative frequency of stomata on fossil leaves i.e., stomatal index can be used to calculate atmospheric CO_2 levels	• Closely related species have very different responses to pCO_2

(continued)

Table 5.2 (continued)

Method	Assumptions	Scientific rationale	Limitations
	• The target plants adjust their stomatal index of leaves to optimize CO_2 uptake • Atmospheric pCO_2 close to the plant is representative of the atmosphere as a whole • The quantitative relationship between stomatal index and CO_2 observed on short time scale applies over evolutionary time • Environmental factors such as irradiance, atmospheric moisture, water availability, temperature, and nutrient availability do not affect the relationship between stomatal index and CO_2 • Stomatal index response to CO_2 of extinct species can be determined or assumed • Tophonomic processes do not affect stomatal index counts • Diagenetic processes do not affect stomatal index counts		• The assumption that short-term response is the same as the evolutionary response is difficult to test • The shape of the calibration curves mean much greater certainty applies to low pCO_2 and short time scales
Boron isotopes in foraminifera: estimated applicability—0–100 million years	• Measured boron isotope ratio is accurate and precise • The equilibrium constant for dissociation of boric acid and boron isotopic fractionation between B(OH) and $B(OH)_4^-$ is well known • Boron incorporation into carbonate is predominantly from borate ion • Boron isotope ratio of foraminifer calcification reflect ambient surface sea water pH • Aqueous pCO_2 is in equilibrium with atmospheric pCO_2 • Habitats of extinct species can be determined • There is no vital effect fractionation in extinct species or it can be determined	Boron isotope ratios in foraminifera or other calcifying organisms give paleo pH from which pCO_2 can be calculated if a value of a second carbonate system parameter such as alkalinity is assumed	• Calculated pCO_2 is very sensitive to the boron isotope ratio of sea water which is relatively poorly known, especially for earlier cenozoic • Effects of foraminiferal preservation are not well understood • Method has been used successfully to reconstruct glacial-interglacial cycles

(continued)

Table 5.2 (continued)

Method	Assumptions	Scientific rationale	Limitations
	• The boron isotope ratio of seawater can be determined • Ocean alkalinity or concentration of DIC can be determined • Sea surface temperature and salinity can be measured • Diagenetic effects are minimal or can be quantified		
Mg/Ca in mixed planktonic foraminifera: estimated applicability—0–65 million years	• Analytical errors are negligible • Mg containing oxide and organic contaminants have been removed by oxidative/reductive cleaning • Sensitivity to temperature in extinct species is similar to modern species • Sea water Mg/Ca is known • Surface water carbonate ion/pH is similar to modern • Foraminifera from clay-rich sequences are well preserved and ratios unaffected by diagenesis	Partitioning of Mg/Ca from sea water calcite shells is temperature dependent Calibration of temperature is based on empirical field and laboratory culturing studies As Mg concentration of inorganically precipitated calcite are an order of magnitude higher than biogenic calcite There is no ice volume influence on sea water Mg/Ca though sensitivity does change with seawater Mg concentration	• Diagenetic recrystallization of foram shells can bias the ratios though the direction of bias is unknown and comparisons with other proxies suggest it is minor • The Mg/Ca is also slightly sensitive to sea water pH • Long-term changes in sea water Mg/Ca on the order of 2–5%/10 million yrs • Must be constrained via models

The use of B isotopes as an indicator for sea water paleo pH has been extended to calculation of the past CO_2 concentration in the ocean surface waters and the atmosphere. The uncertainty in the estimates of CO_2 concentration obtained include the fractionation of B isotopes during incorporation in $CO_3{}^{2-}$ shells, effects of diagenesis, and the changing B isotope ratios in ambient sea water. For samples older than 15 M yrs, which is the residence time of B in the oceans, this approach becomes less reliable.

With the discrepancies and uncertainties discussed above and further summarized in Table 5.2, the study of long-term C cycle change becomes less reliable compared to the C-cycle studies analogous to ice-core records of the late Quaternary periods. The study of C cycle change which uses the geological proxies requires geochemical models to test the hypothesized relationships among the global fluxes and reservoirs. Nevertheless, four primary proxy CO_2 methods: (i) carbon isotopes in soil carbonate and OM, (ii) boron isotopes in foraminifera, (iii) alkenone (plankton biomarker) carbon isotope, and (iv) stomata density of plant leaves have undergone comparatively further development to minimize the uncertainties and have been used successfully to evaluate C cycle changes of the Cenozoic Era; (Mason-Delmotte et al. 2013). Although proxy estimates are highly indirect, concurrent estimates of Pliocene CO_2 concentration by different proxies agree well, with the difference of only about 50 ppmv, and shows that during the warm Pliocene atmospheric CO_2 concentration was between 330–400 ppm similar to current concentrations (Seki et al. 2010). The multi-proxy data also show that the decrease in values similar to pre-industrial times—275–285 ppm occurred between 3.2 and 2.8 M yrs and coincided with intensification of Northern Hemisphere glaciation (Seki et al. 2010).

Although there are difficulties in defining CO_2 regime, paleogeography and climates of these older times in order to quantitatively use this information and constrain future climate, over the Phanerozoic Eon, glaciation and colder temperatures seems to have occurred only when the atmospheric CO_2 is inferred to be at the end of its range. Temperature reconstructions in those geologic times are derived from ^{18}O isotopes as well as Ca: Mg in foraminifera and alkenones. Indicators for the identification of presence of continental ice on Earth show that the planet was in general, ice free during the geological history, suggesting generally warm temperatures. Major expansion of Atlantic glaciations starting at about 35–40 M yrs ago is considered to be a response, in part, to declining atmospheric CO_2 concentration. Natural changes in the balance of fluxes in the global C cycle have caused the past variations in the atmospheric CO_2 concentrations over geologic time scales. Variations in CO_2 are one of many factors that have affected climate change over the course of Earth history, and the geological record is consistent with the current understanding of the radiative contribution of CO_2 to climate change.

5.4 Precambrian History of Carbon Cycling

Throughout the major part of the Earth's 4.6 billion years (Bn yrs) history, element cycles have been driven mainly by solar radiation and water and rock cycles which are natural control factors (Berner and Berner 1996). The early atmosphere contained very little O_2 and the C cycle did not resemble its modern form. It is generally agreed that the composition of the atmosphere, the oceans, and the biosphere has changed dramatically over time during the Earth's history. The O_2 was absent or present in very low concentrations in the atmosphere before 2.4 Bn yrs, CO_2 and CH_4 were much more abundant than now, and oceans were largely anoxic (Holland 2005). The emergence of life about 3.8 Bn yrs ago added another factor affecting element cycles, leading to increase in O_2 concentration. The first rise of atmospheric O_2 concentration occurred during the 'Great Oxidation Event' between 2.4 and 2.0 Bn yrs (Holland 2005). By around 2.0 Bn yrs ago, the biosphere had developed to the point at which the photosynthesis played an important role, and molecular O_2 began to accumulate in the atmosphere at the expense of CO_2. The second O_2 rise occurred between 0.8 and 0.5 Bn yrs (Holland 2005). The second atmospheric O_2 concentration rise is generally attributed to rapid emergence of higher organisms, with atmospheric O_2 reaching at times higher concentrations than present and atmospheric CO_2 varying continuously but much higher than that in the present (Berner and Kothavala 2001).

The detailed C cycling during Precambrian and the causes of rise in atmospheric O_2 concentration during Great Oxidation Event is highly debated, however (Holland 1999; Lasaga and Ohmoto 2002; Kasting 2013). Change in the redox state of volcanic gases has been proposed as a trigger for the oxidation state of the atmosphere (Kasting et al. 1993). It is suggested that loss of H_2 from the top of the reducing atmosphere resulted into increase in overall oxidation state of the Earth and the mantle, leading to an overall increase in the fraction of O_2 of the volcanic gases and changes in the redox state of the atmosphere (Holland 2002). The earliest forms of life are thought to have fundamentally different modes of C cycling, in which organic synthesis and metabolism occurred without the production and consumption of O_2. Early forms of life may have cycled C through redox reactions involving hydrogen (H_2), S, Fe, or non-biotic compounds (Rasmussen 2000). Discovery of cyanobacteria biomarkers dating back to 2.7–2.8 Bn yrs ago in sedimentary rocks (Brocks et al. 1999) prior to great oxidation event support this hypothesis. The origin of the photosynthesis is also attributed to cyanobacteria, which appears to have evolved hundreds of millions of years prior to the rise in atmospheric O_2 (Des Marais 2001). During the period of transition to oxygenated conditions, the O_2 produced by photosynthesis may have been consumed by reactions which reduced other compounds.

The quantitative rise in atmospheric O_2 and mechanisms involved are still not well understood, but it has been suggested to be the result of evolving differentiation of the Earth's mantle and crust, changes in oxidation state of volcanic gases, episodes of tectonic activity, hydrogen escape from upper atmosphere to the space, increased productive forms of life and more effective subaerial weathering (Holland 2002; Kasting 2013). High concentrations of atmospheric CO_2 and/or CH_4 are necessary in order to offset the lowered luminosity of the Sun during this period. The atmosphere contained high concentrations of CO_2 and CH_4 during these times, and these processes also affected C cycling. Declining concentration of CO_2 and CH_4 is generally hypothesized as causes of global glaciation during these early years, and increasing CO_2 has been hypothesized as a cause of subsequent deglaciation (Pavlov et al. 2003). The mechanisms of gradual geologic C cycle change spans a broad range of timescales and include many complex and poorly understood relationships and feedbacks. They also present challenges in understanding of cycling of many other elements in addition to C.

5.5 Carbon Cycling During Phanerozoic

At the beginning of Phanerozoic Eon (541 M yrs ago) the atmospheric O_2 concentration was 75% of its present value and CO_2 concentration was higher, about 10 times the pre-industrial concentration of 280 ppmv (Berner 2004; Holland 2005). During Phanerozoic Eon (541–0 M yrs) the Earth passed through two major cycles. Since the Late Precambrian the Earth has also passed through two major cycles with the period in the range of ~300 M yrs. Both of these cycles contain one phase in which the atmosphere is enriched with CO_2 leading to greenhouse climates, and another phase in which the CO_2 is depleted, leading to icehouse climates susceptible to development of ice sheets (Fig. 5.2; Fischer 1984; Holland 2005). In the initial phase of these super cycles, the larger lithospheric plates broke up and the supercontinents were rifted and dispersed. Enhanced release of CO_2 led to increase in atmospheric CO_2 concentration and warm greenhouse climate (Holland 2005). The first of the cycle extended from the end of Cambrian to the end of Devonian (~485–359 M yrs ago). Appearance of vascular terrestrial plants about 380–350 M yrs created a new CO_2 sink in addition to silicate weathering. Plant materials resistant to decomposition were also buried in marine and terrestrial sediments, thereby accelerating the removal of atmospheric CO_2 (Crowley and Berner 2001). The second cycle extended from the beginning of Jurassic throughout Eocene (201–34 M yrs ago) in which mantle convection lessened and supply of volcanic CO_2 was reduced and also the atmospheric CO_2 concentration declined, resulting into a climatic icehouse state (Holland 2005). Nearly all coal, which is the most abundant fossil fuel, owes its origin to burial of higher land plants mostly during Carboniferous era (359–300 M yrs) and more recent times.

The most complete geochemical models of atmospheric CO_2 track the exchange of C between buried organic and inorganic C and the atmosphere—oceans (Berner and Kothavala 2001; Wallmann 2001; Kashiwagi and Shikazono 2003). High concentration of the atmospheric CO_2 in the early Phanerozoic is followed by a large drop to low concentrations during Permian-Carboniferous. The primary reason for this drop is hypothesized as the rise of large vascular land plants which accelerated the weathering of Ca and Mg silicates and later led to burial of increased

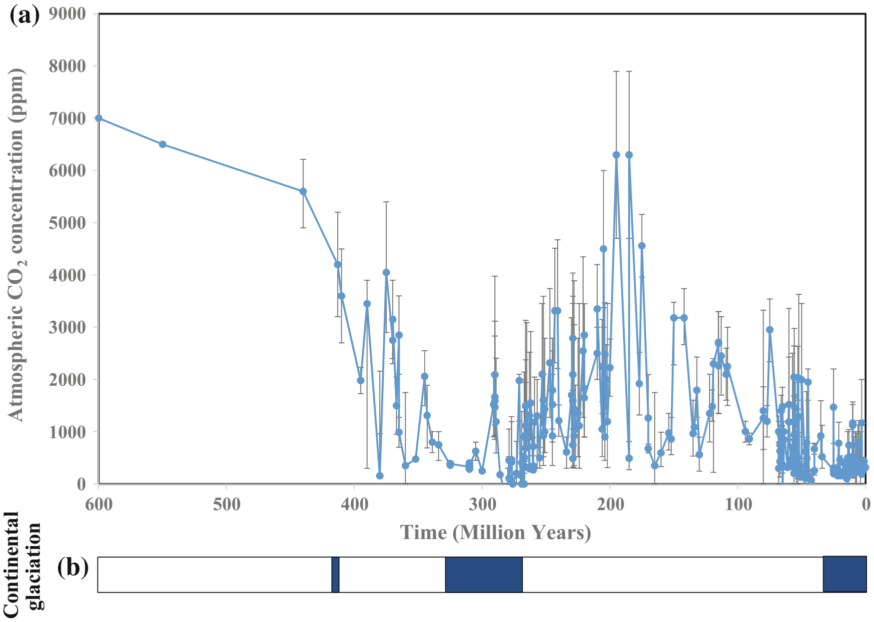

Fig. 5.2 The atmospheric CO_2 concentration (**a**) and presence of continental glaciation (**b**) during phanerozoic estimated by different geologic proxies. Data obtained from Royer et al. (2004), Crowley (1998)

quantities of OM in sediments (Berner 2004). At the end of Permian, the atmospheric CO_2 concentrations rose to high values during the early Triassic. After this, the CO_2 remained high in the Mesozoic and began a gradual decline, punctuated by short and medium-term excursions, which extended into Cenozoic reaching rather low concentrations compared to Phanerozoic. Contributing to this drop was increased mountain uplift in the Cenozoic and continual increase in solar radiation throughout Phanerozoic the solar radiation exerted a major influence on weathering rate, helping to bring about an overall long-term decline in CO_2. Changes in Phanerozoic CO_2 correlate well with paleoclimate. Times of minimal CO_2 coincide with the two most widespread and long-lasting glaciations of the Phanerozoic (330–270 M yrs) (Fig. 5.2; Royer et al. 2004).

5.6 Carbon Cycling During Cenozoic

5.6.1 Carbon Cycling and Climate of the Early Cenozoic

The past 66 M yrs of Earth history is known as Cenozoic Era. It encompasses large climate variations, including the transition from ice-free warm planet to the onset of

Pleistocene, a large-scale continental glaciation and worldwide diversification of grasses with the evolution of C_4 photosynthesis that currently dominate savannahs, rising to ecological dominance 3–8 M yrs ago (Edwards et al. 2010; Beerling and Royer 2011). Such change is not unexpected, because the primary forces that drive long-term climate—Earth's orbital geometry and plate tectonics have also been in perpetual motion. The Cenozoic climates prior to 2.6 M yrs were mostly warmer than the modern period and was associated with higher atmospheric CO_2 concentrations. However, beyond the reach of the ice cores, about 1 M yrs ago, data on atmospheric CO_2 concentration determined by geological proxies becomes much more uncertain.

5.6.2 Carbon Cycling and Climate of the Warmer Greenhouse World

The ecosystems through Cenozoic can be loosely subdivided into the warm greenhouse world (66–34 M yrs ago) period and the modern icehouse world (34–0 M yrs ago) (Fig. 5.3; Norris et al. 2013). During the warmer Cenozoic (66–34 M yrs), multiple geological proxy evidence suggest much warmer mean global temperature and poles with little or no ice (Zachos et al. 2001; Royer 2006). Indicators for the presence of continental ice on Earth show that the planet was mostly ice-free, indicating generally warm global temperatures. The extreme case is Paleocene early Eocene period, when CO_2 concentration and global temperature reached a long term maximum and also associated with atmospheric CO_2 concentrations above 800 ppmv between 50–34 M yrs and higher than 1500 ppmv between 66 and 50 M yrs (Fig. 5.4; Beerling and Royer 2011). The sea surface temperatures were unusually warm from 55 to 45 M yrs, with tropical sea surface temperatures as high as 30–34 °C, and deep temperatures of 8–12 °C during early Eocene compared to 1–3 °C in the modern ocean, and also high latitude temperatures were also unusually warm with above-freezing winter polar temperatures without large ice sheets (Cramer et al. 2011; Pross et al. 2012).

Through the Cenozoic, the well-known long-term decrease in atmospheric CO_2 concentration and subsequent cooling is believed to be the result of global decrease in volcanic degassing, which was coupled with tectonically enhanced increases in silicate weathering, carbonates sedimentation, and elevated OC burial (Raymo et al. 1988; Raymo and Ruddiman 1992; France-Lanord and Derry 1997; Wallmann 2001). The Cenozoic era is also characterized by a deep sea cooling of ~ 12 °C believed to have been mostly forced by changes in the atmospheric GHGs composition (Hansen et al. 2008). Changes in atmospheric CO_2 concentration has been documented by proxy data (Pagani et al. 1999a, 2005b) and modeling (Wallmann 2001). However, lack of constraint to the ancient C cycle makes it difficult to determine the significant processes that controlled this evolution of C cycle.

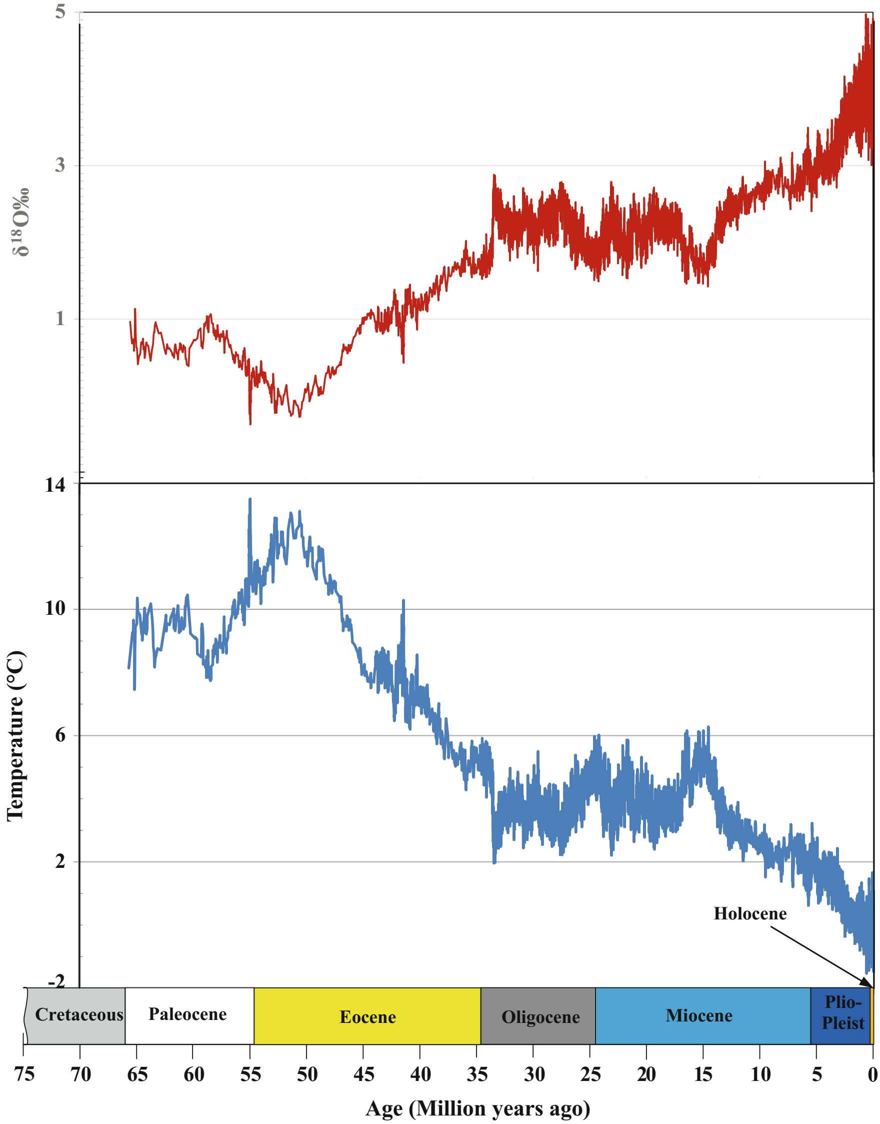

Fig. 5.3 Temperature estimate and $\delta^{18}O$ for the past 65 million years. Modified from Zachos et al. (1993, 2001, 2008)

Volcanic emissions were particularly high during parts of Paleocene and Eocene 40–60 M yrs ago, but diminished afterwards. Lack of water storage in large polar ice sheets caused sea level to be ∼50 m higher than modern ocean, creating extensive shallow-water platforms (Lyle et al. 2008; Pross et al. 2012). During early Eocene, tectonic connections between Antarctica, South America, and Australia

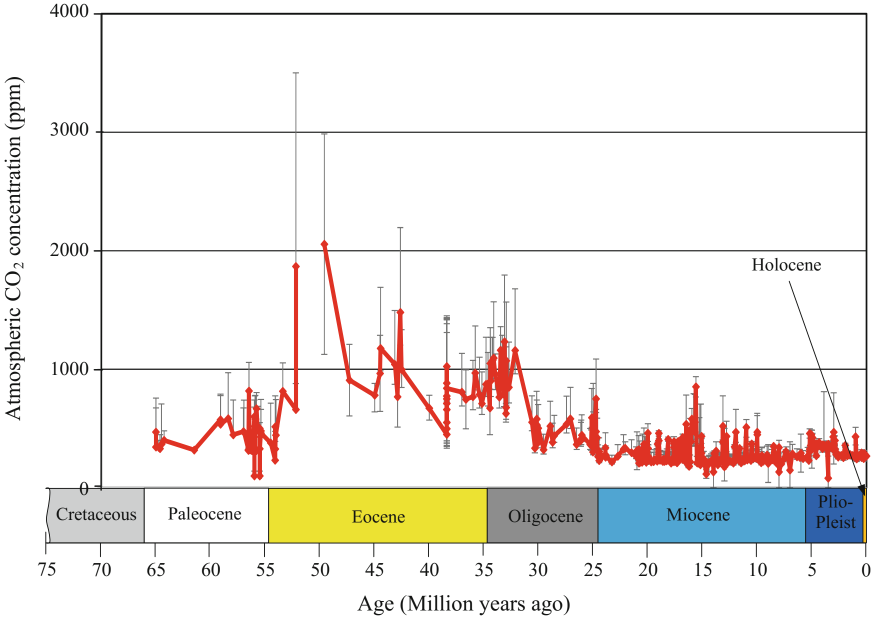

Fig. 5.4 The atmospheric CO_2 concentration for the past 65 million years reconstructed from marine and terrestrial geological proxies. *Data from various sources* Pagani et al. (1999a, b, 2005a, b, 2010, 2011), Royer et al. (2001a, b), Beerling et al. (2002, 2009)

allowed warmer subtropical waters to extend much closer to Antarctic coastline and prevent formation of extensive ice cap (Pross et al. 2012), while also limiting the extent of ocean mixing and nutrients delivery to plankton communities in Southern Ocean (Salamy and Zachos 1999). Arctic Ocean was also anoxic as a result of tectonic barriers and strong pole-ward storm, occasionally containing substantial freshwater quantities (Pagani et al. 2006).

5.6.3 Paleocene-Eocene Thermal Maximum Event

On shorter timescales, atmospheric CO_2 concentration and temperature can change rapidly as demonstrated by series of events known as hypothermal in the early Cenozoic. One of this distinct period of extreme global warming occurred close to the boundary between Paleocene and Eocene ~55.5 M yrs (Sloan and Morrill 1998; Westerhold et al. 2007, 2012; McInerney and Wing 2011; Huber and Caballero 2011; Fig. 5.3). This abrupt climatic condition termed as Paleocene-Eocene Thermal Maximum (PETM), which was first identified in 1991 (Kennett and Stott 1991) occurred during a time of generally warm planet due to the greenhouse effect climatic conditions but stands out against the background of warmer temperature as an abrupt and short-lived spike in global temperatures (Fig. 5.2). The benthic foraminifera indicate deep ocean water temperatures of about 10 °C (Zachos et al. 2001) compared to current temperatures between 2 and 3 °C (Martin et al. 2002). The atmospheric CO_2 concentrations as high as 4000 ppm have been estimated from different proxies during PETM (Lowenstein and Demicco 2006; Beerling and Royer 2011; Mason-Delmotte et al. 2013, Fig. 5.2b). The atmospheric CO_2 during the late Paleocene is assumed to be 400–600 ppm based on several proxies of the atmospheric CO_2 concentration (Royer et al. 2001b; Royer 2006; Pagani et al. 2006; Hilting et al. 2008; Breecker et al. 2010). The PETM event is most intensively studied abrupt warming event in the geologic record (Kennett and Stott 1991; Dickens et al. 1995; Thomas and Shackleton 1996; Thomas et al. 2002; Zachos et al. 2003, 2005; Sluijs et al. 2007; Meissner et al. 2014) with the objective of providing insights into the global C cycle, climate system, and biotic responses to abrupt increase in atmospheric CO_2 concentration, since it provides an analog for future climate and environmental changes, given the current trends of anthropogenic CO_2 emissions (Meissner et al. 2014).

It was an abrupt warming event that lasted for 200,000 years and involved profound changes in the global C cycle, ocean chemistry, as well as climate, and led to major perturbations of both terrestrial and marine ecosystems (Zachos et al. 2003; Tripati and Elderfield 2005; McInerney and Wing 2011; Meissner et al. 2014). The PETM event is characterized by a uniform globally warm temperatures estimated at 5–8 °C warmer (Bowen et al. 2015), superimposed on an already warm Earth (Zachos et al. 2003, 2005; Bowen et al. 2004) with relatively rapid onset and a gradual recovery on a hundred thousand year timescale. The onset was accompanied by intense dissolution of carbonate of the sea floor throughout the deep sea (Zachos et al. 2005) which indicates ocean acidification, as well as anomalous negative excursion in $\delta^{13}C$ of the surface reservoir—ocean, atmosphere and biosphere ranging from negative 3 to negative 6‰ (Kennett and Stott 1991; Koch et al. 1992). This phenomena which could only have been generated by rapid and massive release of ^{13}C-depleted C in the form of CO_2 and/or CH_4 to the ocean-atmosphere system at the event's onset (Thomas et al. 2002; Pagani et al. 2006). One possible source for the C is the release of CH_4 gas hydrate from marine systems (Dickens et al. 1995). However, the released CH_4 would have oxidized relatively quickly to CO_2 in the water column and/or the atmosphere (Schmidt and Shindell 2003; Carozza et al. 2011; Kessler et al. 2011).

The PETM event is of particular importance because of the magnitude of C injected into the atmosphere and ocean, which can be used to understand the future climate impact and environmental changes if the atmospheric CO_2 emissions continues on their current trajectory (Ridgwell and Schmidt 2010; Zeebe and Zachos 2013). The event is also of interest considering the evidence for widespread CH_4 leakage from the sea floor in both Arctic Ocean (Biastoch et al. 2011; Westbrook et al. 2009; Berndt et al. 2014) and the northern margin of the Atlantic seaboard of the USA (Skarke et al. 2014). These releases may be related to the warming of ocean waters associated with the current anthropogenic climate change, necessitating further investigation on the long-term stability of marine clathrates under the ongoing anthropogenic warming of the ocean.

The source(s) of C and the mechanism(s) of release remains the subject of intense debate (Dickens 2003; Storey et al. 2007; Cui et al. 2011; McInerney and Wing 2011; Wright and Schaller 2013; Zeebe 2013; Bowen et al. 2015). Hypothesized sources include: (i) thermal dissociation of marine CH_4 hydrates, (ii) widespread oxidation of organic C, (iii) igneous intrusion into organic-rich sediments, (iv) CO_2 outgassing from lava flows, (v) thermogenic CH_4, (vi) Antarctic permafrost/peat, and (vii) bolide impact. The causes of C release also remains a matter of discussion (Nisbet et al. 2009). Estimates of the total amount of C released and whether it was single or in multiple phases of C release also remains unresolved. At the low end, Zeebe et al. (2009) constrained the initial C release to <3000 Pg C. However, Zachos et al. (2005) estimated a total release of >4500 Pg C based on extent of sea floor CO_3^{2-} dissolution. Panchuk et al. (2008) refined this amount to >6800 Pg C based on dissolution estimates simulated by the geochemical model. Reconstruction of Arctic hydrology also supported the high release estimate (Pagani et al. 2006). Assessment of C isotope composition of soil nodules collected from two boreholes from the Bighorn Basin in Wyoming USA formed around the time of PETM event identified a C isotope excursion immediately preceding the PETM event interpreted as pre-release of C at a smaller magnitude and shorter duration prior to main pulse of the PETM (Bowen et al. 2015). Inclusion of precursory C release in the PETM C cycle model suggests the source of C associated with both events as two pulses of CH_4 released from marine gas hydrates termed as clathrates. Precursory release of >0.9 Pg C yr^{-1} directly to the atmosphere estimated to last for ~2000 years (i.e., >1800 Pg C), and the main pulse of CH_4 associated with the PETM event as a feedback to CH_4 released during the pre-onset excursion was proposed (Bowen et al. 2015). Also, the length of time separating the pre-onset excursion and the PETM event (about 2000 years) is roughly the time believed to be required for the bottom-water warming to be transmitted into the gas hydrate stability zone in marine sediments (Zeebe 2013). If Bowen et al. (2015) hypothesis is correct, then it provides geological evidence for future strong clathrate feedback to current anthropogenic global warming.

Other evidences also indicates ~4 °C warming prior to the onset of C isotope excursion, suggesting a multiple releases and possibly multiple sources of C (Sluijs et al. 2006; Secord et al. 2010). Other estimations based CO_3^{2-} dissolution and C isotope excursion yields a C release of 4300 Pg for CH_4 clathrates and >10,000 Pg C for all other sources (McInerney and Wing 2011). According to modeled carbonate dissolution, a pool of >10,000 Pg C release is needed to explain the observed warming (Panchuk et al. 2008).

The PETM event was characterized by a large changes in ocean chemistry and biotic response with profound shifts in biotic communities on both land and sea lasting for about 200,000 years (McInerney and Wing 2011). Even before the Paleocene-Eocene transition was recognized as a major perturbation of climate and C cycle, this interval was known as a major interval of largest benthic foraminiferal extinction in the past 90 M yrs, removing 30–50% of benthic foraminiferal diversity (Thomas 1989, 2003). The benthic foram extinction has been attributed to increased corrosivity of deep waters, lower O_2 concentrations, changes in food supply, and higher temperatures (Thomas 2003, 2007).

The PETM event was accompanied by rapid shifts in $\delta^{13}C$ and $\delta^{18}O$ observed in species specific marine foraminiferal carbonate (Thomas et al. 2002) and terrestrial carbonate (Koch et al. 1995). It was also characterized by increased Mg:Ca ratios in plankton and benthic foraminifera (Zachos et al. 2003; Tripati and Elderfield 2005); pole-ward migration of tropical and sub-tropical marine plankton (Crouch et al. 2001). A profound shift in biotic communities, including terrestrial plant species (Wing et al. 2005) and terrestrial mammals migration across northern high latitudes (Bowen et al. 2002; Smith et al. 2006) have also been identified. In addition to the dispersal event, the decrease in body size (i.e., dwarfing) of the terrestrial fauna has been observed—probably as a result of increase in temperature and/or declining productivity (Smith et al. 2009). It was a period of major biotic restructuring that lasted for more than 100,000 years (Zachos et al. 2005). Based on interpretation of several proxies, atmospheric concentrations of CO_2 and CH_4 increased sharply and the ocean temperatures increased by 3–10 °C (Zachos et al. 2005). Therefore, the changing climatic and oceanographic conditions drove rapid adjustments in the geographic ranges of most forms of life regardless of habitat, trophic level or prior distribution, as it is currently occurring as a result of global climate change.

The time required for recovery of Earth system offers useful information about the recovery of Earth system from current anthropogenic C emissions. Following the body of C isotope excursion which lasted for $\sim$100,000 years, C isotope values and temperature returned to near pre-PETM values over $\sim$100,000 years (Murphy et al. 2010). Three mechanisms have been proposed for the drawdown of CO_2: (i) increased storage in the terrestrial biosphere (Bowen and Zachos 2010), (ii) increased marine export production (Torfstein et al. 2010), and (iii) enhanced silicate weathering on land with increased preservation of CO_3^{2-} in the ocean (Kelly et al. 2010). The initial C isotope recovery was rapid, occurring over 30,000 years, thereafter likely required a process that preferentially sequestered ^{13}C-depleted C such as burial of OM in soils and peats (Bowen and Zachos 2010).

Although the interest in PETM event research is, in large part, stimulated by the similarity to the current GHG emissions and the associated C cycle perturbation as a result of the ongoing anthropogenic CO_2 emissions, and due to the belief that this event parallels the current and future anthropogenic CO_2 emissions trajectory, the differences between the two have become much clear: The C release that caused the C isotope excursion at the PETM took at least 8000–10,000 years, roughly 15 times longer than any anticipated anthropogenic C release. This much slower rate of C addition to the atmosphere translates to much less severe acidification and CO_3^{2-} dissolution of the ocean sediments surface, less severe consequences for the terrestrial and marine organisms, and also climate impact during the PETM event than the coming centuries.

5.7 Carbon Cycling and Climate of the Cool Icehouse World

The atmospheric CO_2 concentration which was ~700–1500 ppmv during the late Eocene and dropped to 400–600 ppmv across Eocene-Oligocene boundary 34 M yrs (Liu et al. 2009). Major expansion of Antarctic glaciations starting around 40–35 M yrs was likely a response, in part, to declining atmospheric CO_2 concentration (DeConto and Pollard 2003) and changes in ocean circulation. Antarctic ice continued to grow further between 34 and 30 M yrs as atmospheric CO_2 concentration declined (Pagani et al. 2011), and significant expanded during Miocene (Lear et al. 2000; Francis et al. 2008) when climate conditions—atmospheric CO_2 and/or insolation passed the threshold (Holbourn et al. 2005; Shevenell et al. 2008). By around 13.9 M yrs the entire Antarctic continent was covered by ice (Lewis et al. 2008). Tectonic separation of Antarctica from Australia first and later from South America (Lyle et al. 2008) resulted into establishment of Antarctic Circumpolar Current which increased the pole-to-Equator temperature gradient, increased upwelling of nutrients and biogenic production in the Southern Ocean which initiated the modern polar ecosystems (Houben et al. 2013).

The growth of polar ice ~34 M yrs produced sea level fall estimated at ~50 m, and later Northern Hemisphere ice sheet at ~2.5 M yrs initiated sea-level fluctuations of up to 120 m (Lambeck and Chappell 2001; Rohling et al. 2010). The Arctic sea also evolved from anoxic lake to a basin with perennial sea ice cover by ~14 M yrs (Backman and Moran 2009). Decrease in CO_2 also caused continental and ocean cooling, with high latitude deep ocean temperatures declining to 4–7 °C between 34 and 15 M yrs, and further polar cooling over the past 5 M yrs (Cramer et al. 2011).

5.7.1 *Transition to Glaciation in Northern Hemisphere*

One of the intriguing challenges which has prompted much research in geologic history of the Earth is to understand the drivers of the fundamental climate change from the past greenhouse world without major polar ice caps to the icehouse that was dominated by the continental ice and vast ice sheets on the southern and northern poles. These changes across major climate threshold holds many clues that can help understand the potential changes the world is undergoing and may undergo in future. Various studies have speculated that the variability in atmospheric CO_2 concentrations may have controlled the past climate transitions (Shevenell et al. 2004; Holbourn et al. 2005). Other mechanisms have also been proposed as the causes of the past climate transitions, including changes in ocean circulation patterns (Haug and Tiedemann 1998), sea ice dynamics (Ashkenazy and Tziperman 2004), orbital driven variation in amount or distribution of insolation (Huybers

2006, 2011), and upper water stratification in tropics and/or high latitudes (Sigman et al. 2004).

Geological evidence from rocks and fossils from continental and marine O_2 isotopes that records the changes in temperature and water masses indicate that the Northern Hemisphere transitioned from localized episodic glaciation events to extensive regional scale glaciation from late Pliocene about 2.75 M yrs ago onwards (Mudelsee and Raymo 2005). Significant tectonic reorganization occurred during the late Miocene, including major tectonic uplift of Himalayas (Fang et al. 2005), the Andes (Garzione et al. 2008), the North American Rockies (Morgan and Swanberg 1985), the East African Plateaus (Yemane et al. 1985) and the Alps (Kuhlemann 2007). Other changes include closure of open Panama gateway between Atlantic and Pacific, restricted Indonesian seaway between Pacific and Indian Ocean, and the end of permanent El Nino in Equatorial Pacific (Bradshaw et al. 2012). Each of these tectonically driven events triggered a major shift in dynamics of the global climate system (Raymo and Ruddiman 1992; Ruddiman 1997). As a result of these changes in both land and Ocean circulation patterns, atmospheric CO_2 concentration decreased to estimated Pliocene concentrations of 275–400 ppmv (Seki et al. 2010).

The Pliocene (5.3–2.6 M yrs) has raised interest because the continental and ocean configuration was almost similar to modern Earth, and because until ~3 M yrs, the climate was warmer than modern Earth by 4 °C in tropics and 10 °C near poles. During the warmest intervals between 3.0 and 3.3 million years about 3 °C globally warmer than the pre-industrial times (Haywood and Valdes 2004; Lunt et al. 2010). This caused sea level to rise by 12–32 m (average of ~20 m, (Ravelo et al. 2004; Miller et al. 2012; Rohling et al. 2014) although CO_2 concentration was almost similar (415 ppm, Pagani et al. 2010). An El Nino-like state existed in the Pacific and lasted several millions of years (Wara et al. 2005). Although most of this warmth is commonly attributed to increased CO_2 concentration (Lunt et al. 2012), simple comparison of temperature change in geological records with CO_2 climate forcing alone are unable to constrain the equilibrium climate sensitivity (Lunt et al. 2010), and lack of sensitivity of climate models prevents a realistic simulation of Pliocene warm climate without artificially introducing an increase of atmospheric CO_2 larger than inferred from geological records of this period (Pagani et al. 2010), suggesting that CO_2 is not the only factor that influenced the regional cooling at the end of the Pliocene. Pliocene represents a warm period in a cold global climate state (i.e., ice house) which started ~50 M yrs ago, while Antarctica started to grow toward 30 M yrs. The atmospheric CO_2 concentration estimated by different proxies during Pliocene range from 190 to 450 ppm (Seki et al. 2010; Beerling and Royer 2011; Badger et al. 2013; Martinez-Boti et al. 2015).

Earth's climate evolution over the last 5 million years since the early Pliocene has been meticulously studied with the main focus of understanding the origin of glacial-interglacial cycles (Crowley 1996; Jansen et al. 2000; Ravelo et al. 2004; Ruddiman 2003b; Fedorov et al. 2013). Early Pliocene was characterized by mean global temperatures 3–4 °C warmer than current, comparable to those predicted for the second half of 21st century (Haywood et al. 2002; Dowsett 2007), suppression of Northern Hemisphere glaciation (Hodell and Channell 2016; Lunt et al. 2010; LaRiviere et al. 2012), 15–25 m higher sea level (Shackleton et al. 1995), enhanced thermohaline circulation, small and emerging Northern Hemisphere ice coverage, and higher atmospheric CO_2 concentration. In the Southern Hemisphere, both East and West Antarctic ice sheets were fully established, however (Dolan et al. 2011). Even within this globally warmer Pliocene world, short lived episodic glaciation events and accompanying sea level fluctuations have been recorded in benthic isotope records before climate deterioration at the end of Pliocene (Lisiecki and Raymo 2005; Miller et al. 2005, 2012). Although the factors influencing the Northern Hemisphere glacial inceptions during Late Pleistocene have been deeply investigated, they are still poorly constrained, and few simulations focusing on a full glacial cycle have not been able to reproduce accurate volume fluctuations without accounting for more precise internal climate feedbacks such as vegetation and dust.

Despite relatively small differences in climate control factors and atmospheric CO_2 concentrations between early Pliocene and modern climatic conditions, Pliocene was markedly different (Fedorov et al. 2006). Paleo-records indicate vast change in climate patterns since 5–4 M yrs which cannot be explained by paralleled 100 ppmv decrease in atmospheric CO_2 concentration during Pliocene, including contraction of the tropical belt and oceanic warm pool (Brierley et al. 2009), emergence of strong temperature gradients along the Equator (Wara et al. 2005), cooling of coastal upwelling zones in the subtropics (Dekens et al. 2008), the shoaling of ocean thermocline (Wara et al. 2005; Steph et al. 2006), and cooling of high latitude and deep ocean (Lawrence et al. 2009; Sosdian and Rosenthal 2009). These observations imply a transition from climate with almost no zonal sea surface temperature gradients and weaker meridional sea surface temperature gradient to a much more pronounced spatial temperature contrast of the modern times. Severe deterioration of global climate in the late Pliocene led to the widespread Northern Hemisphere glaciation ~2.75 M yrs. Northern Hemisphere glaciation was a gradual process that began around 3.6 M yrs, suggesting one or more tectonic mechanism that operate over long time periods. Uplift of Tibetan Plateau, leading to weathering induced atmospheric CO_2 removal has been suggested as one of such mechanism (Mudelsee and Raymo 2005). Modeling indicates that glaciation of Greenland during late Pliocene is mainly controlled by decrease in atmospheric CO_2 (Lunt et al. 2008a). Pliocene is therefore, characterized by long-term increase in global ice volume and decrease in temperature from 3.3–2.6 M yrs (Lisiecki and Raymo 2005; Mudelsee and Raymo 2005; Fedorov et al. 2013), which marks the onset of continental scale glaciations in the Northern Hemisphere.

The gradual cooling that followed is believed to have led to establishment of modern temperature patterns and the onset of widespread Northern Hemisphere glaciation. Even though the changes which are believed to occur during Pliocene are not representative of future warmer period, nevertheless, the warmer Pliocene period provides an ideal time interval to understand the climatic processes of warm anthropogenic greenhouse effect of the future because this recent geological past features geographical configurations, ocean currents, and both marine and terrestrial ecosystems almost similar to current. Also, until ~3 M yrs, the climate was warmer than current by ~4 °C in tropics and ~10 °C near poles. This caused sea level to rise by ~20 m (Ravelo et al. 2004) although CO_2 concentration was almost similar at 415 ppm (Pagani et al. 2010). The general opinion is that Northern Hemisphere glaciation developed as gradual global cooling transition starting at about 3.15 M yrs BP with gradual intensification, culminating into major Arctic glaciation at 2.74 M yrs BP (Ravelo et al. 2004; Bartoli et al. 2005). The onset of glacial inception occurred 2.7 M yrs ago as evidenced by geological proxies. The initial cause and mechanisms for the intensification of Pleistocene glaciation is still debatable. However, some of the suggested mechanisms include: (i) the closure of Central American Seaway (Lunt et al. 2008b); (ii) changes in orbital parameters (iii) declining atmospheric CO_2 levels, (iv) tectonic uplifting of Greenland—Scotland Ridge, (v) variation of sea floor spreading rates, (vi) termination of Pliocene permanent El Nino conditions, and (vii) tectonic uplift in the Arctic region.

It is generally accepted that the primary driver of the glacial-interglacial cycles is the Earth's orbital configuration and the resulting variations in insolation (Hays et al. 1976). Other factors such as the CO_2 and CH_4 concentration, which have corresponding climate lags of several thousands of years (i.e., ~5000 yrs), are thought to drive the ice sheet growth and decay similar to that of insolation or to be driven by the ice sheets fluctuations (Ruddiman 2003b). Oceans are considered as amplifier of those oscillations, since their thermal inertia is large and may have delayed the climate response to external forcings variations (Knorr and Lohmann 2003). The mechanisms driving transition between glacial-interglacial periods are poorly understood. Although insolation changes seems to trigger interglacial periods, current full general circulation models (GCMs) cannot reproduce those transitions.

Model studies show that Greenland glaciation is mainly controlled by a decrease in atmospheric CO_2 concentration during late Pliocene. However, under the inferred Pliocene CO_2 concentrations of 380–400 ppm, the three popular proposed causes—climatic shift associated with the tectonically driven closure of Panama Seaway (Keigwin 1982; Haug and Tiedemann 1998) and termination of permanent east-west temperature gradient across equatorial Pacific referred to as El Nino state (Wara et al. 2005; Haywood et al. 2005; Philander and Fedorov 2003) failed to initiate such extensive glaciation, and only by lowering CO_2 concentration from 400 to 280 ppm did modeling succeeded in understanding the initiation of full scale glaciation of Greenland (Lunt et al. 2008a). However, the sea surface temperature gradients at low latitudes change little while temperature in the warm pool rises by 2–3 °C, confirming that minor atmospheric CO_2 decrease of 50–100 ppm could not have induced the observed structural climate change even with high Earth system climate sensitivity (Lunt et al. 2010; Fedorov et al. 2013), highlighting the urgent need to confirm what the CO_2 content of the atmosphere was before and after the inception of Greenland glaciation and the health of Greenland ice sheet under current CO_2 concentration.

During late Pliocene the gradual cooling occurred over several million years and climate mainly oscillated mostly following 40,000 year obliquity cycles from 2.8 M yr (Lisiecki and Raymo 2005, 2007). Long-term trends of climatic cooling and increasing glacial cycle amplitude during Plio-Pleistocene suggests a significant changes in the dynamics of the climate system. The dominant period of Pleistocene glacial cycles changed from 40,000-year cycles to 100,000-year glacial cycles for yet unknown reasons (Hönisch et al. 2009). Based on 2.1 M yr sea surface CO_2 concentration, boron isotopes in planktic foraminifer shells, the atmospheric CO_2 partial pressure (pCO_2) was relatively stable before mid-Pleistocene climate transition. Change in periodicity was accompanied by a gradual increase in value and amplitude of the O_2 isotopic composition of benthic foraminifer shells suggesting a total ice volume increase as deep water temperature decrease over the mid-Pleistocene transition (Lisiecki and Raymo 2005).

5.7.2 Carbon Cycle Variations During Glacial-Interglacial Cycles

The ancient air trapped in ice cores provide a unique archive as the best record of ancient atmospheric CO_2 concentration to complement instrumental data and provide a direct record of the past atmospheric well-mixed GHGs concentration (Joos and Spahni 2008; Köhler et al. 2011). The ice cores hold information in three distinct forms: (i) the isotopic composition of the water molecules themselves are proxy for the local temperature at the time of the ice formation (Johnsen et al. 1992; Jouzel et al. 2007b), (ii) many impurities trapped in snowflakes and snow surface provide information about the environmental parameters such as occurrence of spikes of volcanic eruptions (Castellano et al. 2005) and aerosol content of the atmosphere (Wolff 2011), (iii) air bubbles at the depth below the close-off depth acts as an archive of stable trace gases that were in the atmosphere at the time of ice formation.

As snowflakes are buried deeper in the firn column they metamorphose and form networks of ice crystals that become less permeable and finally form a totally impermeable ice matrix in which air bubbles are trapped, which occurs at depths ranging from 60 to 100 m depending on the site (Wolff 2011). The trapped air bubbles are almost perfect stored sample of the overlying air, which their contents can be analyzed for major as well as trace gas components. Therefore, ice cores provide direct evidence of past variations in atmospheric concentrations of GHGs and other gases, aerosols, and dust. These variations in atmospheric chemistry reflect variations in global C cycling and past climate, and have become powerful tool for constraining the Quaternary history of the global C cycle and climate. The ice cores also provide a direct record of past climate change that can be closely correlated with the C cycle variations and offer a compelling evidence for associations between climate and the C cycle over broad range of timescales.

The limitations of the samples of air trapped in bubbles are: (i) gases that have a short lifetime such as photochemically produced radicals are missing from the air bubbles, (ii) air close-off depth has typically an age of few decades depending on the time it takes for air to diffuse to close-off depth. Therefore, the trapped air is older than the air above the snow surface but much younger than the ice that encloses it. As a result, the air trapped at a particular depth represent a range of ages reflecting times of bubble closure. Ice core samples are therefore dated by applying age-difference correction relative to closing ice which is estimated from models confirmed by observation of modern firn layers and extrapolated to past climatic conditions (Schwander et al. 1997), (iii) fractionation occurs in the firn column due to gravitational effects that concentrate heavier molecules at the bottom of the column. This fractionation must be corrected for when studying the isotopic composition (Elsig et al. 2009).

The ice cores extending to the depth that exceed 3 km deep from Antarctica and providing trace gases concentrations and climate record are currently available for the period extending to 800,000 years, covering eight glacial/interglacial cycles (Augustin et al. 2004; Jouzel et al. 2007b; Loulergue et al. 2008; Lüthi et al. 2008; Schilt et al. 2010). The climate during this time period is characterized by the patterns of extended cold glacial period marked by gradual cooling interrupted by an abrupt warm interglacial conditions which recurs at approximately 100,000 years frequency (Augustin et al. 2004; Lisiecki and Raymo 2005; Jouzel et al. 2007b), and is seen ice core records (Petit et al. 1999), terrestrial, as well as in marine sediments (Imbrie et al. 1993) demonstrated by temperature anomalies reconstructed from deuterium isotope (^{2}D) for the glacial-interglacial period (Fig. 5.5). The relatively brief warm periods are accompanied by disappearance of

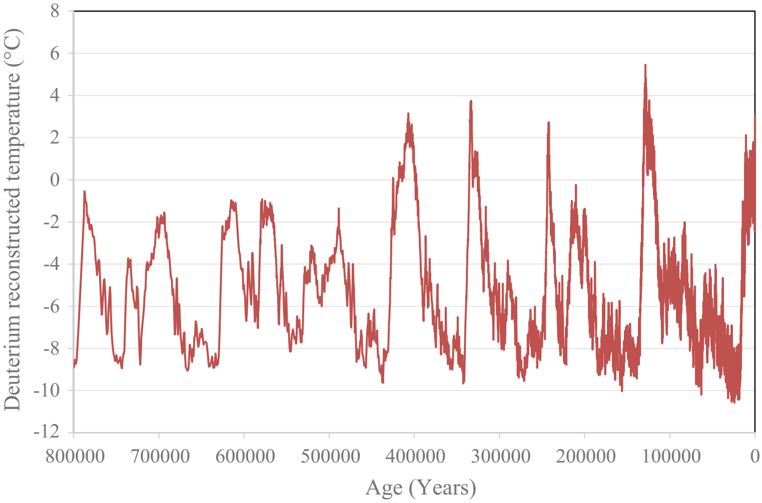

Fig. 5.5 Temperature variation during glacial-interglacial period reconstructed from deuterium content of the EPICA Dome C ice core from Antarctica. *Data source* Jouzel et al. (2007a, b), available online at www.ncdc.noaa.gov

large ice masses in Northern Hemisphere and sea level rising accordingly. This periodic switch within the system from buildup of ice to its rapid disappearance gives rise to asymmetric cycles termed as terminations (Broecker and Vandonk 1970). The most recent four cycles show long glacial with short interglacial periods and a temperature range of around 10 °C between warmer than cold glacial periods for the Antarctica as seen in ice cores (Fig. 5.5; Petit et al. 1999). However, the cycles preceding 450,000 years BP show relatively longer but cooler interglacial periods with longer proportion of warmer periods compared to the most recent four cycles (Augustin et al. 2004).

The CO_2 concentrations from ice cores show exactly the same pattern (Lüthi et al. 2008) and indeed has remarkably similar characteristics to Antarctic temperature as reconstructed from the deuterium isotope ratios of water in the ice cores (Fig. 5.6). The correlation of the CO_2 concentration with Antarctic temperature during the 800,000 years period of existing ice cores has an r^2 of 0.82 (Fig. 5.7; Lüthi et al. 2008), indicating strong coupling between CO_2 concentration and Antarctic temperature. At the times of minimum glacial temperatures, the CO_2 concentration dropped to typically 170–200 and then rapidly rose to concentrations ranging from 240 to 290 ppmv during interglacial periods (Fig. 5.6). Prior to 420,000 years, interglacial CO_2 concentrations were generally lower, and ranged from 240 to 260 ppmv, these were also accompanied by much cooler temperatures, but after 420,000 years, the interglacial CO_2 concentration was 270–290 ppmv (Lüthi et al. 2008).The lower CO_2 concentration by ∼40 ppmv during weaker interglacial periods between ∼420,000 and 800,000 years also coincided with cooler interglacial temperatures (Fig. 5.6; Lüthi et al. 2008).

The low CO_2 concentrations observed in ice cores that formed during glacial periods agree with the earlier measurements in the ice cores collected from

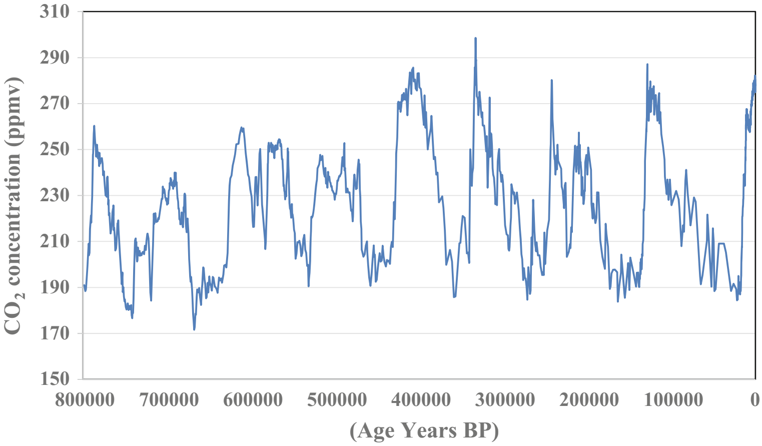

Fig. 5.6 Carbon dioxide mixing ratio from Antarctic ice cores over the last 800,000 years. Modified from Petit et al. (1999), Lüthi et al. (2008). Data available online at www.ncdc.noaa.gov

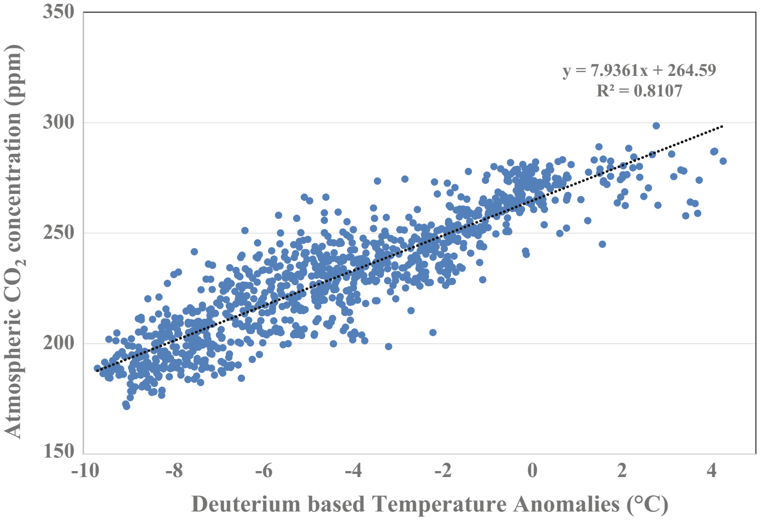

Fig. 5.7 Correlation between the atmospheric CO_2 concentration and global temperature anomalies reconstructed from deuterium isotopic proxy for the past 800,000 years as recorded in Antarctic ice core

Antarctica and Greenland (Berner et al. 1980; Delmas et al. 1980; Stauffer et al. 1988). The deuterium temperatures and isotopic record of Antarctic and Greenland ice can be linked with well-known global climate variations across Hemispheres by direct matching the sediment isotope records (Shackleton 2000, 2001) and oxygen isotope variations in the ice core air and deep marine sediments cores (Bender and Battle 1999; Shackleton 2000). Concentrations of CO_2 seems to be responsible for 30–50% of the observed variations seen in climate (Genthon et al. 1987; Petit et al. 1999). The similarity between the CO_2 mixing ratio and Antarctic temperature extends to the smaller multi-millennial-scale variations during glacial periods (Ahn and Brook 2008) and to the pattern of change during terminations (Monnin et al. 2001). The ice cores reveal a range of natural variations in atmospheric CO_2 during glacial/interglacial period, but never exceeded 300 ppm, providing evidence that the current atmospheric CO_2 concentrations are higher than they have been at any time during the past 800,000 years.

Ice cores recovered from Antarctic ice sheets also have revealed that the atmospheric CO_2 concentration during Last Glacial Maximum (LGM) at 21,000 years was about a third lower than that during the subsequent interglacial (i.e., Holocene) period that started at 11,700 years (Fig. 5.8; Delmas et al. 1980; Neftel et al. 1982; Monnin et al. 2001). In addition, Vostok ice core record indicate that minimum and maximum calculated temperatures were similar for the four last glacial-interglacial cycles, and the maximum temperature during interglacial was similar to that of Holocene prior to any human influence. Other temperature proxies, including isotopic composition yielded very high statistical correlation

Fig. 5.8 Carbon dioxide mixing ratio for the last glacial termination and holocene. Modified from Monnin et al. (2004). Data available online at www.ncdc.noaa.gov

with CO_2 concentrations and local temperatures (Petit et al. 1999). There is an excellent agreement among glacial/interglacial CO_2 concentrations from diverse locations in the Antarctica (Fischer et al. 1999). The reasons behind a well-documented synchronous change in surface temperature and atmospheric CO_2 concentration are still unclear.

Antarctic ice cores are generally considered more suitable for CO_2 measurements because of their lower temperatures and lower concentration of impurities, which minimizes the risks of analytical artifacts. In contrast, Greenland ice has higher levels of reactive impurities. Therefore, there is no reliable ice core CO_2 concentrations from Greenland that can be compared in detail with Antarctic CO_2 concentrations. Combination of higher carbonates, lower pH, and higher concentration of organic impurities in the ice leads to in situ production of CO_2 for Greenland ice cores (Anklin et al. 1995; Smith et al. 1997), while in Antarctic ice cores no such artifacts have thus far been observed. In addition, Antarctic ice cores have low scatter, high resolution CO_2 concentration samples in ice bubbles (Indermuhle et al. 1999; Tschumi and Stauffer 2000; Monnin et al. 2001; Lüthi et al. 2008). There is also high consistence of Antarctic ice core CO_2 concentration from different locations, and very good agreement of ice core CO_2 data with atmospheric CO_2 measurements in the overlapping interval with direct instrumental measurements between 1958 and 1975 (Fig. 5.9; Etheridge et al. 1996; MacFarling Meure et al. 2006). The agreement among CH_4 measurements in cores from Antarctica and Greenland ice discussed in Chap. 7, but it suggest strongly that Antarctic ice core CO_2 record can be considered as a record of global glacial/interglacial changes in climate and atmospheric CO_2 composition. Likewise, deuterium temperature record and other Antarctic and Greenland records of stable

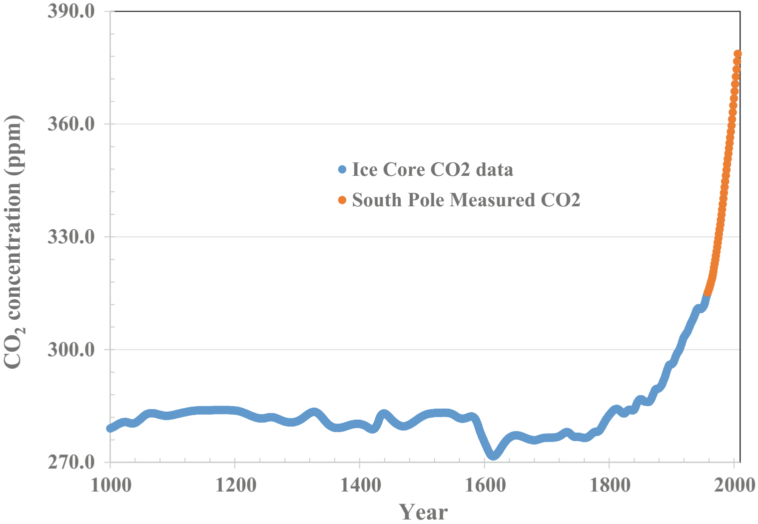

Fig. 5.9 Carbon dioxide concentration at Antarctica for the last 1000 years. *Blue diamond* is ice core CO_2, while *red squares* are the instrumental measurement from South Pole station. Modified from Etheridge et al. (1996). Data available online at NOAA (www.ncdc.noaa.gov/data-access/paleoclimatology ice core record, and www.ncdc.noaa.gov/ south pole instrumental measured CO_2 mixing ratio)

isotopes in ice can be linked to well-known global climate variations by directly matching the similarities among ice core and marine sediment isotope records (Shackleton 2001) and by correlation between $\delta^{18}O$ variations in the ice core and marine sediments (Shackleton 2000).

Comparison of temperature proxies and CO_2 during the last glacial-interglacial transition suggests that Antarctic temperature started to rise before atmospheric CO_2, confirming the view that natural CO_2 variations constitutes a feedback for the primary cause of climate variation during the glacial/interglacial cycles (Shackleton 2000). It is broadly accepted that succession of glacial-interglacial cycles is primarily driven by cyclic changes in orbital parameters that control the seasonal and latitudinal distribution of solar radiation reaching the Earth's surface which is induced by variation of shape of Earth's orbit (i.e., insolation), tilt of its spin axis (i.e., obliquity) and precession (i.e., change in orientation of rotational axis of the Earth) generally termed as Milankovitch cycles (Imbrie et al. 1992; 1993; Kawamura et al. 2007; Cheng et al. 2009; Lisiecki 2010; Paillard 2010; Berger 2013). The influence of orbital parameters on global climate was first hypothesized and calculated by Milutin Milankovitch (1879–1958). Milankovitch theory proposes that ice ages are triggered by minima in summer insolation (i.e., the amount of solar radiation reaching the Earth by latitude and by season measured in W m^{-2}) near 65°N, enabling winter snowfall to persist all year and therefore, accumulate to build northern hemisphere ice sheets. There is a strong evidence that the cycles of cold and warmer periods during ice age are linked to Milankovitch cycles that change the amount of solar radiation received at each latitude in each season.

Although these periodic cycles reoccurring at 100,000 (eccentricity), 41,000 (obliquity), and 23,000 (precession) years interval have been identified in many paleoclimate records, there is no consensus on exact mechanisms by which the variations in Earth's orbital configuration affect the climate (Ganopolski and Calov 2011). Models and other analyses of global climate suggest strongly that the insolation changes directly attributed to orbital causes are not sufficient to explain the magnitude and relative importance of periodicities observed in differences between glacial and interglacial climate (Imbrie et al. 1993; Shackleton 2000; Wallmann 2014). The alteration between glacial and interglacial states has been attributed to a complex set of processes that involve orbital forcing (i.e., changes in incoming solar radiation originating from variations in Earth's orbital parameters as well as changes in its axial tilt) and internal interactions and feedbacks in the climate system (Archer et al. 2000; Sigman and Boyle 2000). Orbital forcing is a well-known phenomenon from precise calculations for its past and future (Laskar et al. 2004).

Change in parameters of the orbit of the Earth around the Sun modifies seasonal and longitudinal distribution of incoming solar radiation at the top of the atmosphere (i.e., insolation, Berger 1978). Past and future changes in insolation can be calculated over several millions of years with a high degree of confidence (Berger and Loutre 1991; Laskar et al. 2004). For the past 800,000 years, the tilt of the Earth axis (i.e., obliquity) has varied between 22.04° and 24.5° with strong quasi-periodicity around 41,000 years, and these changes have impact on seasonal constants. The obliquity also modulate annual mean insolation at any latitude, with opposite effects at high and low latitudes. Change in the Earth's orbit around the Sun are considered as the pacemaker for glacial-interglacial cycles (Berger 1978), but these changes must be amplified by climate feedbacks in order to explain large differences in global temperature and ice volume, and the relative abruptness of the transitions between glacial and interglacial periods (Berger et al. 1998; Clark et al. 1999). Biogeochemical cycles play an important role for the amplification of orbital cycles, and model simulations suggest that the direct radiative forcing of CO_2 and CH_4 atmospheric concentrations could have contributed up to 50% of the observed glacial surface temperature changes at the global scale (Shin et al. 2003). Other major factors involved in maintaining cold conditions during glacial period include the water vapor feedback, high albedo of the continental ice sheets, high albedo of non-forested regions at high latitudes, and reflections of short wave radiation by greatly enhanced atmosphere current of mineral dust (Claquin et al. 2003).

However, it is a matter of debate why the much weaker 100,000-year cycles produce stronger climatic cycles by direct forcing than stronger precessional around 20,000-year or obliquity at 41,000 years cycles that causes larger changes to insolation (Shackleton 2000; Berger 2013). The mechanisms that amplify a small change into large global climate change is not well understood. It has been proposed that the unusual behavior of the insolation patterns is strongly amplified by ice sheet dynamics (Imbrie and Imbrie 1980), ocean circulation (Imbrie et al. 1993), and the global C cycling (Shackleton 2000). Biogeochemical cycles play important role of amplifying any orbital changes, and model simulations suggest that atmospheric CO_2 and CH_4 concentrations contributed up to 50% of the observed glacial-interglacial surface temperature differences at a global scale (Shin et al. 2003). Other factors involved in maintaining cold conditions during glacial periods include water vapor feedback, high albedo of the continental ice sheets, and the reflection of shortwave radiation by the enhanced atmosphere content of mineral dust (Claquin et al. 2003) as a consequence of reduced vegetation cover (Werner et al. 2002). The variations in Earth's orbital parameters are also amplified by changes in atmospheric CO_2 concentration and ocean circulation, which plays an important internal feedback role. Variability in CO_2 concentration over the last several hundred thousand years covaries with variability in proxy records, including global ice volume (Lisiecki and Raymo 2005), Antarctic temperature (Parrenin et al. 2013), and deep ocean ventilation (Lisiecki et al. 2008). It is therefore, proposed that the duration and the intensity of cold and warm periods is strongly amplified by ice sheets dynamics, ocean circulation, and/or the global C cycle (Imbrie et al. 1993; Shackleton 2000; Wallmann 2014).

Overall, the exact mechanisms controlling glacial/interglacial CO_2 change remain unresolved. A number of mechanisms are reasonably understood, but no single feedback mechanism appears to be sufficient to explain the full magnitude of C cycle variations during glacial-interglacial cycles. The mechanisms which have been proposed to account for C cycle variation during glacial-interglacial cycles include (i) increase in terrestrial vegetation in interglacial periods acting to remove CO_2, while the increase in sea surface temperatures leads to less CO_2 solubility in the ocean and increase the atmospheric CO_2 concentration. However, taken together with the effects of changing sea level, these better quantified effects almost tends to cancel each other out, and leaves about 100 ppm of CO_2 change observed from glacial-interglacial cycles still unexplained. (ii) reduced land carbon in glacial times as revealed by $\delta^{13}C$ record of ocean waters preserved in benthic foraminiferal shells (Ciais et al. 2012; Bird et al. 1996), (iii) lower sea surface temperatures which has been suggested from temperature reconstructions to average 3–5 °C cooler compared to the Holocene (Archer et al. 2000), (iv) reorganization in ocean circulation and sea ice during glacial periods which promoted the retention of dissolved inorganic C in the deep ocean (Shackleton 2000), (v) lower sea level and increased salinity (vi) iron fertilization as demonstrated by higher rates of dust deposition, resulting into increased marine productivity and lower glacial CO_2 (Röthlisberger et al. 2004).

Most of the proposed explanations center on changes in ocean circulation and ventilation of the deep-ocean, or ocean biogeochemistry—i.e., removal of C through sinking as a result of enhanced biological productivity. Modeling and observation allows limit to be placed on such mechanisms, e.g., the impact of Fe fertilization in certain regions of the ocean which has been constrained by models studies (Bopp et al. 2003) and by observation of periods in the ice core record when dust concentrations were low but CO_2 remained low (Röthlisberger et al. 2004). The currently accepted view is that no single mechanism will explain the CO_2

changes observed, but quantifying the different processes involved will improve modeling of the mechanisms that may be expected to partition increased CO_2 between the atmosphere, land, and ocean under future conditions. In general, the search for mechanisms driving the observed glacial-interglacial changes has led to the identification of range of processes that contribute to the control of atmospheric CO_2 concentrations and climate.

5.8 The Last Glacial Termination and Holocene Carbon Cycle Variations

Between ~24,000 years ago and modern period, the large ice sheets covering most of Canada and parts of Europe and Asia melted away, Earth warmed by ~5 °C, sea level rose by ~120 m, rainfall patterns shifted, and vegetation patterns changed, sometimes abruptly. This natural climatic shift is a continuation of complex variation in Earth's orbital parameters and complex feedback that governed transition from glacial to current interglacial state discussed above which are not well characterized. One of the most important of these feedbacks which has been well-documented and characterized is the change in atmospheric CO_2 concentration. Ice core record of polar ice have shown that ~17,500 years ago, atmospheric CO_2 concentration started to rise from ice age concentration of ~180 ppmv, reaching ~265 ppmv by early Holocene (Fig. 5.8; Monnin et al. 2001). The last glacial maximum approximately 19,000 and early Holocene, 11,000 years ago, every component of the climate system underwent large-scale change as the world emerged from the ice age. This time of dramatic global change was triggered changes in insolation, with changes in ice sheets, greenhouse gas concentrations, and other amplifying feedbacks that produced distinctive regional and global responses, such as sea level rise, and abrupt climate change that produced regional climate signals superimposed on those associated with global warming. The Earth entered the current inter-glaciation with near the pre-industrial GHG concentrations and relatively stable climates.

The Holocene Epoch is the current interglacial period which started at 11,700 years ago following the transition from the last glacial maximum. The evolution of the atmospheric CO_2 concentration during this period is known with high certainty from ice core measurements. The atmospheric CO_2 decreased by about 7 ppmv from 265 ppmv between 11,000 and 7000 years, followed by an increase of 20 ppmv until the onset of the industrial era in 1750 (Fig. 5.8; Indermuhle et al. 1999; Flückiger et al. 2002; Monnin et al. 2004; Elsig et al. 2009). Ice cores records from Taylor Dome C indicate that CO_2 concentration decreased from 270 ppmv at 10,500 years to 260 ppmv at 8000 years, then gradually increased to about 285 ppmv by 1000 years BP (Indermuhle et al. 1999, Flückiger et al. 2002). Overall, the centennial variations of up to 10 ppm in CO_2 have been recorded (Flückiger et al. 2002; Monnin et al. 2004; MacFarling Meure et al. 2006).

Variations in atmospheric CO_2 concentrations were typically small compared to glacial-interglacial changes of typically 100 ppm (Sigman and Boyle 2000; Lüthi et al. 2008), and much smaller compared to modern increase after the Industrial Era. Even though they are small in magnitude, these variations are useful in understanding the role of natural forcing of CO_2 during the Holocene interglacial climate conditions.

Understanding historical C cycle during Holocene have two major advantages in learning how Earth and the climate system may evolve in the future: (i) this period provides examples of the operation of range of processes under boundary conditions (e.g., configuration of continents, ocean gateways, and ocean circulation changes) similar to current conditions, (ii) there are access to more detailed and reliable record of what actually has occurred than can be obtained for earlier times, for example, ice core records from Antarctica and Greenland (Andersen et al. 2004) which contain C cycling and climate record and also concurrent data on climate and forcing mechanisms that have a global reach.

The atmospheric $\delta^{13}CO_2$ was −6.39 to −6.46‰ (average = −6.45‰) between 24,000 and 17,500 years ago, followed by rapid depletion of 0.3‰ between 17,500 and 14,000 years, which coincided with 60 ppmv increase in atmospheric CO_2 concentration. This change has been attributed to release of CO_2 from previously isolated deep-ocean reservoir that accumulated C as a result of oxidation of organic detritus sinking from the ocean surface waters (Schmitt et al. 2012). This is also supported by the decrease in radioactive ^{14}C in the atmosphere about the same time (Broecker and Barker 2007; Burke and Robinson 2012). Between 17,000 and the beginning of Holocene 11,700 years ago, $\delta^{13}CO_2$ remained fairly constant, followed by slow $\delta^{13}CO_2$ enrichment between 12,000 and 7000 leading to maximum value of −6.33‰ around 6000 years ago (Indermuhle et al. 1999; Schmitt et al. 2012). This rise is attributed to regrowth of terrestrial biosphere which preferentially removes ^{12}C from the atmosphere. This mid-Holocene maximum declines slightly to reach a value of −6.35‰ at 500 years ago (Elsig et al. 2009). Although small compared to recent anthropogenic changes in atmospheric chemistry, the Holocene variation provide important information regarding the interactions among climate and the global C cycle.

The decrease in atmospheric CO_2 in early Holocene and the 20 ppm increase during the last 7000 years leading to Industrial Era is the result of a subtle balance of range of processes. The mechanisms underlying the observed 20 ppmv increase in CO_2 concentration over the last 7000–8000 years have been a matter of intensive and ongoing debate (Ruddiman 2003a, 2007). During three last interglacial periods prior to Holocene, CO_2 did not increase, and this has led to hypothesis that preindustrial CO_2 increase is actually the result of an early anthropogenic activities of early land use change and forest clearing for cultivation (Ruddiman 2003a; 2007). However, several lines of evidence have been used to counteract this hypothesis: (i) human activity was not globally intense enough in earlier millennia to have such a large effect, (ii) the hypothesis is not consistent with C isotopic data (Siegenthaler et al. 2005; Elsig et al. 2009), (iii) reasonable explanation for increase in CO_2 concentrations are available (Joos et al. 2004; Broecker and Stocker 2006;

Elsig et al. 2009; Schmitt et al. 2012; Brook 2012). Resolving the cause of CO_2 increase during Holocene remains important due to suggested hypothesis that the rise in CO_2 may have stave off the inception of the next glacial stage (Ruddiman 2003a).

Proposed drivers of atmospheric CO_2 changes during Holocene include both oceanic and terrestrial processes. Oceanic processes centers around carbonate chemistry and OM decomposition in deep-ocean, including: (i) shift in oceanic carbonate sedimentation from deep sea to the shallow waters due to sea level rise into continental shelves which causes accumulation of $CaCO_3$ on shelves and coral reef growth, a process that releases CO_2 to the atmosphere (Ridgwell et al. 2003; Kleinen et al. 2010), (ii) carbonate compensation as a response to release of C from deep ocean during deglaciation and the buildup of terrestrial biosphere in the early Holocene (Elsig et al. 2009; Menviel and Joos 2012), (iii) release of CO_2 from deep-ocean resulting from warming and decomposition (Schmitt et al. 2012), and (iv) a 0.25 °C increase in global sea surface temperature (SST) and related changes in CO_2 solubility (Menviel and Joos 2012). Proxies for carbonate ion concentration in the deep sea and a decrease in $CaCO_3$ preservation in equatorial Pacific sediments supports the hypothesis that the ocean was the source of CO_2 to the atmosphere during the Holocene (Anderson et al. 2008; Yu et al. 2010). Proposed terrestrial processes include regional forest clearing and biomass burning (Stocker et al. 2011), orbitally forced climate variability including mid-Holocene warming of high latitudes of northern hemisphere which caused changes in vegetation distribution and terrestrial C storage (Schurgers et al. 2006; Schmitt et al. 2012; Brook 2012). The CO_3^{2-} compensation mechanism due to land C uptake during the termination (18,000–11,000 B.P.) and early Holocene also contribute significantly to atmospheric CO_2 rise after 7000 B.P. The CO_3^{2-} compensation of earlier land uptake and CO_3^{2-} deposition influence atmospheric CO_2 and $\delta^{13}CO_2$ in similar way. The magnitude of these two processes cannot be distinguished from the atmospheric records.

5.9 Carbon Cycling During the Most Recent Past

Law Dome is the ideal site for studying changes over the last few centuries because of its high snow accumulation rate. It has been possible to compare data form the ice just below the close off depth with the atmospheric measurements from South Pole over recent decades since the gas concentration determined from ice just below the close off depth fall on the atmospheric gases concentration curve (Fig. 5.9). In addition, measurements of CO_2 concentration have been made at several Antarctic sites for this period and demonstrate that: (i) the increasing CO_2 concentration trends seen in atmospheric dataset began in the early 19th century (ii) the increase from the typical value of the AD 1000–1800 period to present is nearly 40% (iii) there were small variations of few ppmv on centennial scales before the industrial Era, and (iv) data from two different sites of Antarctica ranging in altitude and temperature from −19 to −44 °C, locations from inland to coastal show similar concentration and trends and rules out any artefact that could affect CO_2 concentration after closure.

The CO_2 concentration rose to near 285 ppm during 13th century AD, then decreased again to ~275 ppm during 16th century AD (Fig. 5.9; Etheridge et al. 1996; Indermuhle et al. 1999). Increases in CO_2 coincides with a maximum in $^{13}CO_2$ at −6.3‰ (Francey et al. 1999; Indermuhle et al. 1999). Variations in terrestrial sources and sinks associated with forest regrowth over abandoned lands and increased C storage especially in Central America are most likely cause of CO_2 and C isotope trends (Kaplan et al. 2011). These changes are also associated with changes in terrestrial C cycling. Simultaneous oceanic CO_2 uptake changes associated with cooling caused by solar irradiance cannot be ruled out however (Trudinger et al. 1999; Joos et al. 1999). Times of slightly increased and decreased CO_2 during the most recent millennium coincides with warmer and cooler period known as 'Medieval Warm Period' and 'Little Ice Age'. Although the significance of these climatic variations remains unclear, the coincidence of CO_2 and climate trends are consistent with understanding of close coupling between climate and C cycling that has emerged from broad range of times, however. The maximum natural rates of change in atmospheric CO_2 during the most recent millennium were at least the order of magnitude smaller than the current anthropogenic rates of change. Also, the natural variations observed in ice core records were much less persistent than the increasing trends of the most recent two centuries. Measurements of CO_2 and its carbon isotopes in firn and in the uppermost sections of ice cores sampled from Siple Station and Law Dome sites in Antarctica show close agreement with record of direct atmospheric measurements (Francey et al. 1999; Neftel et al. 1985; Friedli et al. 1986; Etheridge et al. 1996). Precise and continuous reliable instrumental measurements of atmospheric CO_2 concentrations began in 1958. These recent observations provide powerful support for the validity of the ice core gas record extending back in geologic time because gas measurements can be closely matched for recent decades with record from firn air and atmospheric measurements (Fig. 5.9).

Several cores from Antarctica provide strong evidence that the atmospheric CO_2 concentration before the onset of anthropogenic influence was 280 ± 5 ppmv. The ice cores also provided a strong evidence that the carbon isotope ratio of atmospheric CO_2 ($\delta^{13}CO_2$) was ~−6.4‰ before the human influence (Friedli et al. 1986; Francey et al. 1999) compared to present value ~−8.2‰, reflecting the influence of ^{13}C-depleted anthropogenic CO_2 added to the atmosphere (Francey et al. 1999). For 800–1000 years prior to industrial revolution of 1700–1800s, the atmospheric CO_2 concentration varied by less than 10 ppm (Prentice et al. 2001). Measurements of $^{13}CO_2$ over the last millennium are consistent with the view that the observed increases are due mainly to fossil fuel CO_2 input, although ^{13}C data alone are not enough to constrain the sources without further information such as emission inventories, the dilution of ^{14}C by ^{14}C-free fossil sources seen in tree rings until first nuclear bomb tests (Suess effect) and changes in the O_2/N_2 ratio of the atmosphere.

Therefore, the primary concern raised by the current increase in atmospheric CO_2 concentration is that the increase much larger than the natural CO_2 variation observed during the most recent 1 million years ago, suggesting perturbation to global carbon cycle which is not represented in recent Earth history. In addition, the degree of global carbon cycle-climate coupling observed in past century is not well represented in past C cycling, suggesting further adjustment of climate in response to ongoing and potential future anthropogenic perturbation of carbon cycling.

5.10 Conclusions

This chapter is a compilation of historical evidence of global C cycling to bridge the gap and set the stage for the understanding of contemporary global C cycling and the associated ongoing anthropogenic perturbations of this cycling. Despite the uncertainties in proxy data and limited distribution and spatial and temporal bias of the paleodata, there is enough evidence to suggest that global C cycling and global climate are linked in many ways throughout the history of the Earth. It is equally apparent that complex interactions of many factors evident from the geologic record defy the simple cause-and-effect, necessitating further collection of paleodata and modeling to continue to improve our understanding of these interactions which are important for understanding the current and future changes in global environment as a result of the past, ongoing, and future anthropogenic perturbations to C cycling. Geological record of the global C cycling has and will continue to reveal array of "abrupt" events that has affected the cycling of C and prolonged cascade of subsequent effects. The current human activities need to be viewed as geologically abrupt event by any standard. Because the ice cores provide such a direct and reliable measure of the past atmospheric composition, they have been a valuable resource for establishing our knowledge of the ancient atmosphere on a firm footing. Most of potential artefacts can be dismissed on the basis of existing measurements, allowing unequivocal statements about non-natural and unusual magnitude and rate of change of CO_2 and C cycling in the past two centuries to be made. Similarly, the coupling of global temperature and radiative forcing associated with concentration of the atmospheric greenhouse gases observed in the last 1 million years, provides a strong support for the association between current increases in GHGs and climate change. Nevertheless, there are some climatic changes observed in the paleodata which are not fully explained and demand further research to establish the mechanisms responsible for these changes.

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Chapter 6
The Modern Carbon Cycle

Abstract The contemporary global carbon (C) cycling involves the exchanges of C within and between the atmosphere, the oceans, and biosphere. The C may be transferred from one reservoir to another in seconds (e.g., the fixation of atmospheric carbon dioxide (CO_2) by photosynthesis) or over millennia [e.g., the accumulation of fossil carbon (coal, oil, gas) through deposition and diagenesis of organic matter (OM)]. The focus of this chapter is on the exchange of CO_2 occurring over the scale of months to a few centuries that are important for the cycling of C over years to decades with the focus on human influence starting from Industrial Era (1750). The cycling of C is important because it approximates the flows of energy around the Earth. The increased use of fossil fuels has led to increase in atmospheric concentration of CO_2 and methane (CH_4), which are the two most important greenhouse gases (GHGs). Addition of GHGs to the atmosphere enhances the greenhouse effect and is the main cause of the global warming. The rate and extent of the warming depend, in part, on changes in global C cycle. The processes responsible for adding C to, and withdrawing it from, the atmosphere are the part of the global C cycling. Some of the processes that add C to the atmosphere such as the combustion of fossil fuels and changes in land use and land management are under direct human control. Similarly human beings can control removal of CO_2 through afforestation and/or reforestation as well as restoration of degraded lands. Others, such as the accumulation of carbon in the oceans or on land as a result of changes in global climate are not under direct human control except through controlling rates of greenhouse gas (GHG) emissions and therefore, climatic change. Because CO_2 is more important GHG, and is expected to continue to be in the future, understanding the global C cycle is a vital part of managing the global climate. This chapter will address, first, the natural flows of C on the Earth, then the anthropogenic sources of C to the atmosphere and the sinks of carbon on land and in the oceans that have kept the atmospheric accumulation of CO_2 lower than it would otherwise have been. Since 1750, the atmospheric concentration of CO_2 has increased by $\sim$44% from 278 ± 5 ppm in 1750 to 400.0 ± 0.1 ppm in 2015, corresponding to atmospheric burden of 260 ± 5 Pg C, largely as a result of fossil fuel combustion, but also from changes in land use and management. At the beginning of Industrial Revolution, the emissions of CO_2 were from land use and land use change; now the emissions are

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largely (~90%) from fossil fuels. The decadal annual rates of fossil fuel CO_2 emissions increased from 3.1 ± 0.2 Pg C yr^{-1} in 1960s to 9.3 ± 0.5 Pg C yr^{-1} for 2006–2015, while land use CO_2 emission decreased from 1.5 ± 0.5 Pg C yr^{-1} to 1.0 ± 0.5 Pg yr^{-1} over the same period. The total global anthropogenic CO_2 emission from 1750 to 2015 is estimated at 600 ± 70 Pg C, of which, fossil fuels and cement production is estimated at 410 ± 20 Pg C and land use change emission at 190 ± 65 Pg C. About 43% of the total anthropogenic CO_2 emission or 260 ± 5 Pg C remained in the atmosphere, while ocean and terrestrial ecosystems sinks were 28 and 27%, respectively. The decadal atmospheric CO_2 growth increased from 1.7 ± 0.1 Pg C yr^{-1} in the 1960s to 4.5 ± 0.1 Pg C yr^{-1} during 2006–2015, with ocean and terrestrial sinks increasing roughly in line with atmospheric increase over the last 50 years. Although there is no clear signal globally of a saturation of land sink strength, there are some indications suggesting that the ocean total CO_2 uptake rate may have declined in recent decades.

Keywords Fossil fuels · Land use change · Carbon balance · Ocean carbon uptake · Residual terrestrial sink · Atmospheric carbon dioxide accumulation

Contents

6.1 Introduction

The global carbon (C) cycle refers to exchanges of C within and between the atmosphere, the biosphere (plants and soil), the ocean, and the sediments and rocks reservoirs. The C cycle encompasses various cycling processes, ranging from the CO_2 uptake by green plants by photosynthesis and its release through respiration, the daily cycle of animal feeding and metabolism, the seasonal cycle of plant growth and decomposition, to geologic cycle of rock mineral weathering, sediment and OM burial, and carbon dioxide (CO_2) degassing. All the processes of C cycling are generally linked by the exchange of CO_2 with the atmosphere. The contemporary C cycle involves the processes occurring over the time scale of months to few centuries. Understanding of the contemporary C cycle and changes in the atmospheric CO_2 is of societal urgency because the cycling of C is an important determinant of the future of the Earth system. The increasing atmospheric CO_2 concentration and the related enhanced greenhouse effect and current and future global warming of the planet Earth associated with increasing greenhouse gas (GHG) concentration has far-reaching consequences. The radiative properties of the atmosphere are strongly influenced by the abundance of well-mixed GHGs which have substantially increased since the beginning of Industrial Era in 1750, primarily due to anthropogenic activities.

The objectives of this chapter are to summarize the current scientific knowledge of the contemporary global C cycling (i.e., anthropogenic C cycling), and CO_2 budget with special reference to changes in the distribution of C in the fast domain during the industrial era—circa 1750. The factors that influence the uptake and release of CO_2 by the land and oceans, the variability and trends of atmospheric CO_2, the underlying sources and sink processes and their perturbations caused by direct human impacts are also examined. The special reference is given to the fate of anthropogenic emission of CO_2 from the fossil fuel combustion and land use change and the C uptake by oceans and land. The contemporary C cycling and C budgets focuses on understanding the processes responsible for adding C to, and withdrawing C from the atmosphere with greater accuracy to guide climate change mitigation policies.

The C may be transferred from one reservoir to another in seconds (i.e., fixation of atmospheric CO_2 into plant biomass through photosynthesis) or over geologic timescale (i.e., formation of fossil C (coal, oil, and natural gas) through decomposition and diagenesis of OM). In this chapter, more emphasis is placed on exchanges of C that are important over the period of years to few centuries. The reservoirs of C that are important for global C cycling in a short timeframe of up to few centuries are the atmosphere, the oceans, and terrestrial biosphere which incorporates vegetation and soils. These reservoirs have natural exchange rates that are fast enough to vary significantly on a short timescales of up to centuries. Of the three reservoirs, approximately 90% of C is located in the oceans. The oceans are able to hold much more C than other reservoirs due to CO_2 diffusion into the ocean and its reaction and dissociation into bicarbonate (HCO_3^{2-}) and carbonate (CO_3^{2-}) ions. The CO_3^{2-} ions are precipitated as $CaCO_3$ (dolomite). The global oceans contain approximately 45 times more C than the atmosphere or 70 times more C than global terrestrial vegetation. Therefore, shifts in the abundance of C among the three reservoirs will have much greater impacts in the atmosphere and terrestrial biota than they have in oceans.

The Earth system is undergoing a large-scale transformation of its components, including the terrestrial biosphere, the atmosphere, and the oceans, that has prompted declaration of new geological epoch of ‘the Anthropocene’ dominated by man-made global changes by some scientists (Steffen et al. 2007; Ruddiman 2013). Humans started to shape the environment as early as approximately 2.5 million years ago as shown by fossil evidence of primitive tools. Human influence grew with growing population and developing technology (Goudie 2006) which culminated in activities during the period starting with the beginning of industrialization, a period which has been considered by some scientists as the onset of Anthropocene (Zalasiewicz et al. 2011; Lewis and Maslin 2015). Since the beginning of Industrial era in 1750, humans have been burning of fossil fuels (coal, oil, and natural gas) as the main source of energy, the process that is transferring large quantities of C from lithosphere and releasing large quantities of CO_2 into the atmosphere (Rotty 1983; Boden et al. 2016). In addition, land use and land cover change (LULCC), especially deforestation and land cultivation, which causes net reduction of terrestrial C storage and release stored soil organic C (SOC) from soils have also become a significant source of anthropogenic CO_2 emissions to the atmosphere in the Industrial Era. As a result, the concentration of atmospheric CO_2 has increased from 278 ± 5 ppm in 1750 to ~400.0 ppm in 2015 (Ciais et al. 2013; WMO 2016). Land C emissions are the second largest aggregate source of the atmospheric CO_2 emissions after fossil fuel burning, accounting for 36% of the total anthropogenic CO_2 emitted to the atmosphere from 1850 to 2000 (Houghton 2007) and about 12% of annual global CO_2 emissions from 2000 to 2010 (Friedlingstein et al. 2010). Indeed, the anthropogenic trends have become evident in the C cycle and its connection with climate that the period since the start of industrial revolution in 1750 is sometimes called the Anthropocene to distinguish it from the proceeding Holocene (Raupach and Canadell 2010). It has been known for over 100 years that changes in greenhouse gas concentration will cause the surface temperature of the Earth to vary (Arrhenius 1896), and a wide range of observations reveals that the sensitivity of Earths' surface temperature to radiative forcing amounts to 3 °C (range 1.5–4.5 °C) per doubling of atmospheric CO_2 concentration (Rohling et al. 2012; Ciais et al. 2013) caused by direct CO_2 and fast-acting feedback mechanisms, mainly atmospheric water vapor and sea-ice and cloud albedo.

The cycling of C is important for three main reasons: (i) C cycling approximates the flow of energy around the Earth—the metabolism of natural ecosystems, human, and industrial systems, (ii) C forms the structure of all life forms on the Earth, making up to 50% of the dry weight of living things. Plants—both terrestrial and marine transforms radiant energy into chemical in the form of C-bonds of sugars, starches, and other forms of OM, and this energy, both in the living organisms or dead OM supports food chains in natural ecosystems as well as human, and some of it is used for energy, heat, and generation of electricity, and (iii) C in the form of CO_2 and methane (CH_4) forms two of the most important GHGs which contribute to natural greenhouse effect that has kept the Earth warm enough to evolve and support life. Without the greenhouse effect, the Earth would be −18 °C rather than +15 °C, and thus inhabitable. Anthropogenic activities in the post-industrial era are increasing GHGs concentration in the atmosphere, however, disturbing the global energy balance with the resultant enhanced greenhouse effect and global climate change. The rate and extent of global climate change depend, in part, on global C cycle. If the rate at which sinks removes C are faster, the CO_2 and CH_4 concentration increase would be less. In contrast, if the rate and processes of removing atmospheric C are diminishing, the atmospheric CO_2 concentration will increase faster than projected on the basis of recent history of the Earth.

Prior to 1750, the atmospheric concentration of CO_2 was relatively stable, ranging between 260 and 285 ppmv for nearly 10,000 years (Indermuhle et al. 1999; Elsig et al. 2009), and anthropogenic perturbations of the global C cycle were relatively small. Since 1750, the concentration of atmospheric CO_2 in the atmosphere has risen from around 278 ± 5 ppmv to ~403.7 ppmv in 2016, as reported for Mauna Loa Observation Station (Keeling et al. 2016). The anthropogenic CO_2 emissions responsible for observed atmospheric CO_2 concentration increase in industrial period are mainly combustion of fossil fuels and forest land clearing and land use change. Some of the processes which remove C from the atmosphere (i.e., sinks), such as establishment of forests and restoration of degraded lands are under direct human control. In contrast, processes such as accumulation of C in the oceans or land as a result of changes in global climate (i.e., feedback between global C cycling and climate) are not under direct control of humans, except by controlling the rate of CO_2 emissions. The atmospheric CO_2 concentration is now higher than any time during the last 1 million years. Because CO_2 is an important GHG, there is a serious concern that the atmospheric CO_2 concentration increase is causing significant warming and other changes in global climate by altering radiation energy and water balances of the Earth's atmosphere.

Between 1750 and 2015, the combustion of fossil fuels—coal, oil, and natural gas together with cement production and gas flaring released 410 ± 20 Pg C from lithosphere reservoir to the atmosphere (Boden et al. 2016; Le Quéré et al. 2016). Land use activities, including deforestation and land cultivation released additional 190 ± 65 Pg C (Le Quéré et al. 2015, 2016). It is estimated that, of the 600 ± 70 Pg released by the anthropogenic activities, 260 ± 5 Pg C have accumulated in the atmosphere (Canadell and Schulze 2014; Le Quéré et al. 2015, 2016). The remaining anthropogenic C has been absorbed by the ocean and in the terrestrial ecosystems. The oceans stored 175 ± 20 Pg C of the anthropogenic origin since 1750, while the terrestrial ecosystems have accumulated 165 ± 70 Pg C since 1750 (Canadell and Schulze 2014; Le Quéré et al. 2015, 2016). Thus, terrestrial ecosystems have not fully compensated the net losses from land use change during the same period. The average net loss from the terrestrial ecosystem from 1750 to 2015 is estimated at 15 ± 45 Pg C.

The budget governing atmospheric CO_2 concentration can be represented as Eq. 6.1:

$$CO_{2(atm)} = CO_{2(FF)} + CO_{2(LUC)} - CO_{2(Land\ sink)} - CO_{2(Ocean)} \tag{6.1}$$

where $CO_{2(atm)}$ is the atmospheric CO_2 fraction, $CO_{2(FF)}$ is the CO_2 emission from fossil fuel burning, cement production, and gas flaring, $CO_{2(LUC)}$ is the CO_2 emission resulting from deliberate human activities on land—including land use change, deforestation, and land cultivation, $CO_{2(Land\ sink)}$ is the uptake of CO_2 by land vegetation and soil sinks, and $CO_{2(Ocean)}$ is the CO_2 uptake of the anthropogenic CO_2 by the oceans.

6.2 Natural Global Carbon Cycle Before the Anthropogenic Influence

The CO_2 is chemically stable and has an average atmospheric residence time of about 5 years before it enters either the ocean or terrestrial ecosystems. However, when CO_2 molecules leave the atmosphere, they are simply swapping palces with CO_2 molecules in the ocean and biosphere. The amount of extra CO_2 that remains in the atmosphere stays there on timescales of centuries. About 20–35% of CO_2 remains in the atmosphere after equilibration with ocean within 2 to 20 centuries Archer et al. 2009). In the absence of anthropogenic CO_2 emissions, C sources and sinks tend to be approximately balanced over multi-decadal timescale, and the atmospheric CO_2 concentration varied in relatively predictable cycles determined by changes in orbital parameters and their influence on climate during glacial-interglacial cycles, and relatively less variable during early Holocene (Chap. 5). There are three major reservoirs with natural exchange rates fast enough to vary significantly on timescale of decades to centuries: the atmosphere, the terrestrial biosphere, and the ocean (Sabine and Tanhua 2010). Of these three reservoirs, approximately 90% of C occurs in the oceans. The total amount of dissolved inorganic C (DIC) in the global ocean water is about 38,000 Pg C, and the amount of organic C is about 700 Pg C, of which, C in living organisms in the ocean amounts to about 3 Pg C (Sundquist et al. 2009; Ciais et al. 2013), the oceans contains about 50 and 70 times more C than the atmosphere and global terrestrial vegetation, respectively. Most of this oceanic C is in the intermediate and deep waters, and only 700–1000 Pg C is in the surface layers of ocean which is in direct contact with the atmosphere (Sundquist et al. 2009). In addition, about 6000 Pg C is contained in ocean floor, surface and reactive ocean sediments with slower turnover rates (Sundquist 1986). The chemistry of sea water and higher solubility of CO_2 drives the distribution of CO_2 at sea-air interface, and about 98.5% of the C in the ocean-atmosphere system is in the ocean. The oceans are able to hold much more C than other reservoirs because CO_2 that diffuses into the oceans forms bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions (Table 6.1).

The biological processes in the ocean have a strong effect on atmospheric CO_2 concentration and global C cycle at all-time scales (Falkowski et al. 1998). Planktonic photosynthesis converts CO_2 into organic C with corresponding decrease in CO_2 partial pressure of the surface water layer. The resulting change in partial pressure

Table 6.1 The distribution of CO_2 in the atmosphere-ocean in parts per thousand molecules

Carbon type	Fraction per thousand molecules
Carbon dioxide (CO_2)	5
Bicarbonate (HCO^{3-})	875
Carbonate (CO_3^{2-})	105
Total	1000
Atmosphere	15
Ocean	985

Source Sarmiento (1993)

gradient at the air-sea interface potentially provides driving force for movement of CO_2 from the atmosphere to the ocean. Conversely, heterotrophic oxidation of organic solutes and particles release CO_2 and potential efflux of CO_2 from the ocean to the atmosphere. Ocean net primary production (NPP) is affected by climate and also participates in complex feedbacks governing climate (Falkowski et al. 1998).

The pre-industrial era fast domain C cycle was close to steady state as evidenced by the relatively small variations of atmospheric CO_2 during Holocene, despite small human-induced emissions caused by changes in land use over the last millennia (Pongratz et al. 2009). Based on estimated atmospheric CO_2 concentration of 278 ± 5 ppm at the beginning of industrial era in 1750 (Etheridge et al. 1996; Ciais et al. 2013), the mass of the atmospheric C was 589 ± 11 Pg C (Sundquist et al. 2009); 1 ppm = 2.120 Pg C (Prather et al. 2012), the vegetation C is estimated at 450–680 Pg C (Prentice et al. 2001), soils contained 2400–3200 Pg C to 3 m depth (Sundquist et al. 2009), of which, the dead OM in litter and soils is estimated at 1500–2400 Pg C to 1 m depth (Ciais et al. 2013). The C in the form of CO_2 is exchanged by natural processes between the atmosphere and the land, and between the atmosphere and ocean. Simplified schematic of the contemporary global C cycling is presented in Fig. 6.1. The natural processes that transfer C among different C reservoirs are photosynthesis, respiration and CO_2 dissolution. The gains and losses are viewed as a cycling process generally called the global C cycle.

6.2.1 Atmospheric Carbon Dioxide Concentration

The modern background or unmanaged CO_2 concentration includes the emission and CO_2 cycling processes that occur in the absence of human influences. Such processes include terrestrial and aquatic photosynthesis and respiration, organic C (OC) burial, rock weathering, volcanism, and C export from soils to rivers and ocean. Moreover, some of these processes are currently much altered by human influences such that it is inappropriate to call them natural. Prior to Industrial Era which began in 1750, the atmospheric CO_2 fluctuated between 180 ppmv and 290 ppmv for at least 2.1 million years (Hönisch et al. 2009; Lüthi et al. 2008, Chap. 5). Over the last 1000 years prior to Industrial Era, the concentration of CO_2 in the atmosphere has varied by less than 10 ppm (Neftel et al. 1985; Etheridge et al. 1996). The earlier atmospheric history of well-mixed GHGs prior to direct instrument measurements have been reconstructed from measurement of air stored in air archive trapped in polar ice cores or in firn (Wolff 2011).

6.2.2 Natural Fluxes of Carbon

The largest natural fluxes of the global C cycle are those that link the atmospheric C reservoir to the biosphere land vegetation and to the ocean (i.e., photosynthesis and

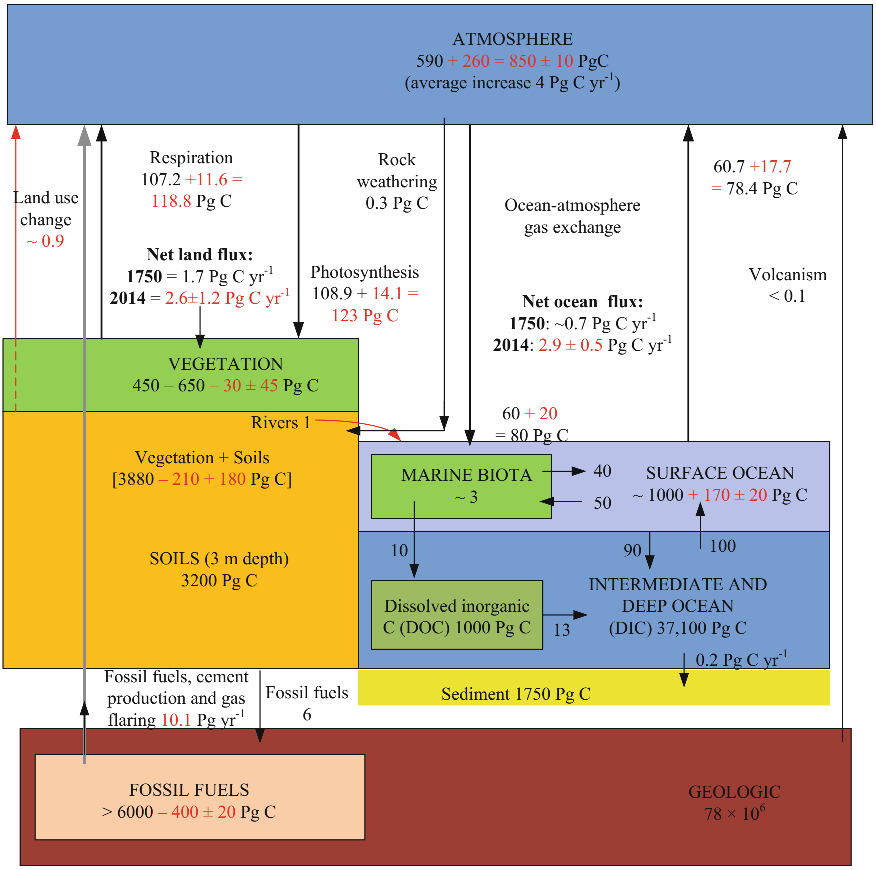

Fig. 6.1 The global carbon cycle before and after the anthropogenic influence. All units are in petagrams (Pg) of carbon. *Numbers in black* are natural (i.e., prior to anthropogenic influence in 1750); while *numbers in red* shows the anthropogenic change by 2014. *Black arrows* indicates fluxes of C (Pg C yr^{-1}). *Sources of data* Ciais et al. (2013), Houghton (2014), Le Quéré et al. (2015, 2016)

respiration, and ocean-atmosphere CO_2 exchange), with annual uptake and release that are close to balanced (Sabine et al. 2004c; Sundquist et al. 2009). Atmospheric CO_2 is cycled naturally through other forms of C over timescales ranging from seconds to millennia and sometimes longer, including export from soils to rivers and oceans and degassing, and rock weathering. Over relatively short timescales of up to 1000 years the most common variations in atmospheric C (i.e., CO_2 and CH_4) involve CO_2 exchange with terrestrial biosphere and oceans, however. In the oceans, the CO_2 needed for photosynthesis is supplied by the atmosphere in DIC form and by CO_2 exchange with air at the ocean surface. Marine plants are the base of ocean food chain, which eventually returns the respired CO_2 to the ocean surface and the atmosphere.

6.2.2.1 Land-Atmosphere Natural Carbon Fluxes

The exchange of CO_2 between the atmosphere and the terrestrial biosphere and oceans drives the terrestrial C cycling. Terrestrial ecosystems exchange CO_2 rapidly with the atmosphere. The inorganic form of C in the atmosphere (CO_2) is fixed by green plants into plant OC using energy from the sun in the photosynthesis process and the fixed C is stored in the plant biomass. It is returned to the atmosphere via respiratory pathways that operate on various timescales: (i) autotrophic respiration by the plants themselves to provide energy for plant growth, (ii) heterotrophic respiration, in which plant-derived OM is oxidized primarily by soil microorganisms to provide microbial energy, and (iii) disturbances such as fire, in which large amounts of OM are oxidized in short periods of time.

The photosynthesis in green plants can be represented by the glucose synthesis in Eq. 6.2:

$$6CO_2 + 6H_2O \leftrightarrow C_6H_{12}O_6 + 6O_2 \tag{6.2}$$

Photosynthesis is the biogeochemical process that acts to transfer C in its oxidized form as CO_2 from the atmosphere to reduced form (OC). The reduction of CO_2 to glucose stores some of Sun's solar energy into chemical bonds of the OM. Glucose, cellulose, carbohydrates, proteins and fats are all forms of OM or reduced C which embody energy and are ultimately derived from the photosynthesis process. Only plants and some microorganisms are capable of reducing CO_2 to produce OM. Therefore, directly or indirectly, photosynthesis provides energy for all other forms of life in the biosphere. The amount of C that is fixed from the atmosphere and converted to carbohydrates during photosynthesis is known as gross primary production (GPP). The GPP of the terrestrial ecosystem before the anthropogenic influence has been estimated at about 123 Pg C yr^{-1} based on ^{18}O isotope measurements of the atmospheric CO_2 (Ciais et al. 1997; Jansson et al. 2010).

Some of fixed C is consumed by plant-eating animals, but much of it is respired by plants and animals to produce energy for plants and animals needed for their survival. The oxidation of OC formed by photosynthesis occurs during the two seemingly dissimilar but chemically identical processes of respiration and combustion. During either process, the chemical energy stored in OC bonds is released. The OC consumed during respiration is converted to CO_2 and recycled back to the atmosphere. About half of the GPP is incorporated into new plant tissue such as leaves, roots, and wood, and the other half is converted back to the atmospheric CO_2 by autotrophic respiration (AR, i.e., respiration by plant tissues) (Lloyd and Farquhar 1996; Waring et al. 1998) estimated at $\sim$60 Pg C yr^{-1}. Respiration is the biotic process that yields energy from OM required for growth and maintenance, but only green plants and some microorganisms are capable of reducing CO_2 to produce OC. About 45–50% of the dry weight of OM is C (Houghton 2014), and OC of terrestrial ecosystems exists in many forms—including living and dead leaves, stems, and roots of plants, animal and microbial biomass, and soil humus. The turnover of OM varies from <1 year to more than 1000 years. The global terrestrial biota C is almost entirely vegetation C, with animals accounting for <0.1% of C in living organisms. All living organisms oxidize OM to produce energy. Respiration by land plants, animals, and microorganisms which provides them with energy for growth, reproduction, and activity, returns 57 ± 9 Pg C yr^{-1} to the atmosphere. The dead plant materials become food source for microorganisms, and also yielding nutrients required for continuing plant life. The decomposition of litter releases 55 Pg C yr^{-1} to the atmosphere as CO_2. Part of the difference between photosynthesis and respiration is burned in wild fires, and part is stored as plant materials or SOC. Annual plant growth is the difference between photosynthesis and autotrophic respiration, which is referred to as NPP. The NPP prior to human influence has been estimated at ~60 Pg C yr^{-1}. Estimated anthropogenic influenced NPP are ~63 Pg C yr^{-1} (Jansson et al. 2010). For many purposes, NPP is the most useful summary of terrestrial plant activity.

Ecologically, NPP is defined as the production of new dry matter by primary producers during a certain period (i.e., the amount of C fixed by photosynthesis available to heterotrophic level in terrestrial ecosystem (Clark et al. 2001; Chapin et al. 2006), it is also the difference between autotrophic photosynthesis and respiration (Schlesinger 1997; Eq. 6.3). The NPP is the major determinant of C sinks on the land and key regulators of processes such as interaction among trophic levels. In the global C cycle, the terrestrial NPP is one of the major C flows and many terrestrial human activities such as agriculture and forestry rely on NPP. From the viewpoint of C balance between the atmosphere and ecosystem, NPP is defined as (Eq. 6.3) (Jansson et al. 2010).

$$\mathrm{NPP} = \mathrm{GPP} - \mathrm{AR}\ [\text{i.e.,}\ {\sim}60 = 120 - 60\,\mathrm{Pg\,C\,yr^{-1}}] \tag{6.3}$$

where, GPP is photosynthetic C assimilation, AR is autotrophic respiration (i.e., metabolic C consumption). The NPP is generally calculated from the relationship between solar energy absorption and biomass production which can be determined by field and satellite remote sensing techniques, and is expressed as (Eq. 6.4):

$$\mathrm{NPP} = \mathrm{LUE_{NPP}} \times \mathrm{PAR} \tag{6.4}$$

where, LUE_{NPP} is the light use efficiency of NPP and PAR is absorbed photosynthetically active radiation (400–700 nm). Terrestrial NPP is not saturated by the present atmospheric CO_2 concentration (Schimel 1995). Therefore, as the atmospheric CO_2 concentration increases, terrestrial plants remain a potential sink for the atmospheric CO_2. The principal C-fixing enzyme in plants is ribulose 1,5-biphosphate carboxylase-oxygenase (Rubisco). In C_3 plants, the activity of rubisco increases with increasing CO_2 concentrations, becoming saturated between 800 and 1000 ppm CO_2. However, the saturation function decreases as CO_2 concentration increases, and terrestrial plants will become less of a CO_2 sink as atmospheric CO_2 continues to increase. In addition, experimental evidence suggests that because of nutrients limitations, NPP will level off at only 10–20% above the current rates—at an atmospheric CO_2 concentrations of 550 to 650 ppm, or double the preindustrial concentrations (Falkowski et al. 2000).

The NPP has been measured in all major ecosystem types by sequential harvesting or by measuring plant biomass. Additionally, estimates through integration of field measurements (Saugier et al. 2001), remote sensing, and atmospheric CO_2 data (Ruimy et al. 1994; Knorr and Heimann 1995) all have estimated global NPP of about 60 Pg C yr^{-1} although there are large uncertainties in all these methods. Recent estimates of NPP vary between 56.4 and 63.6 Pg yr^{-1} (average = $\sim$63 Pg C yr^{-1}) (Field et al. 1998; Ito 2011; Running 2012). The NPP is what fuels the non-green plant world and provides food, feed, fiber, and fuel for both natural ecosystems and human. It is the key parameter of the biosphere that affects plant growth, biogeochemical cycling, biodiversity, carrying capacity of heterotrophic organisms, and ecosystem resilience. As a result, almost all C fixed in NPP is returned to the atmospheric CO_2 through: (i) heterotrophic respiration (Rh) by decomposers—bacteria and fungi feeding on dead tissue and root exudates and (ii) herbivores respiration, and (iii) combustion in natural or human set fires. In addition to returning CO_2 to the atmosphere, decomposers of OM also supplies other nutrients from the biomass required for continuing plant life. A small proportion ($\sim$4 Pg C yr^{-1}) is oxidized through fires. The sum of autotrophic and heterotrophic respiration makes up the ecosystem respiration (ER). The sum of autotrophic and heterotrophic respiration is the total respiration or ER. In a steady state, the net flux of C between atmosphere and terrestrial ecosystems [i.e., net ecosystem production (NEP)] is approximately zero. However, year to year variations in photosynthesis and respiration, including fires may depart from this long-term balance by as much as 5–6 Pg C yr^{-1}.

$$\mathrm{NEP} = \mathrm{GPP} - \mathrm{AR} - \mathrm{Rh}; = \mathrm{NPP} - \mathrm{ER} = \sim 0 \tag{6.5}$$

When other losses of C are accounted for—including fires, harvesting and removal of biomass, and eventually burning or decomposition, erosion and export of dissolved or suspended OC by rivers to the ocean, the remaining C (if any) is the net biome production (NBP, i.e., the C accumulated by the terrestrial biome). Recent estimates of NBP have ranged from -1.4 ± 0.7 Pg C yr^{-1} (Prentice et al. 2001). By definition, for an ecosystem in steady state, Rh and other C losses would balance NPP, and NBP would be zero. In reality, human activities, natural disturbances, and climate variability alter NPP and Rh, causing transient changes in the terrestrial C pool, and thus non-zero NBP. If the rate of C input (NPP) changes, the rate of C output (Rh) also changes in proportion to the altered C content, but there is a time lag between changes in NPP and changes in slower responding C pools. For an increase in NPP, NBP is expected to increase at first, but later to relax towards zero over a period of years to decades as the respiring pools catches up (Mackey et al. 2013). This has implications to the capacity of lands and terrestrial C sequestration to remove atmospheric CO_2 and store it in vegetation and soils in that, the capacity of terrestrial C sequestration is limited by the amount previously depleted by land use change. It has been estimated that if all C released by LULCCs

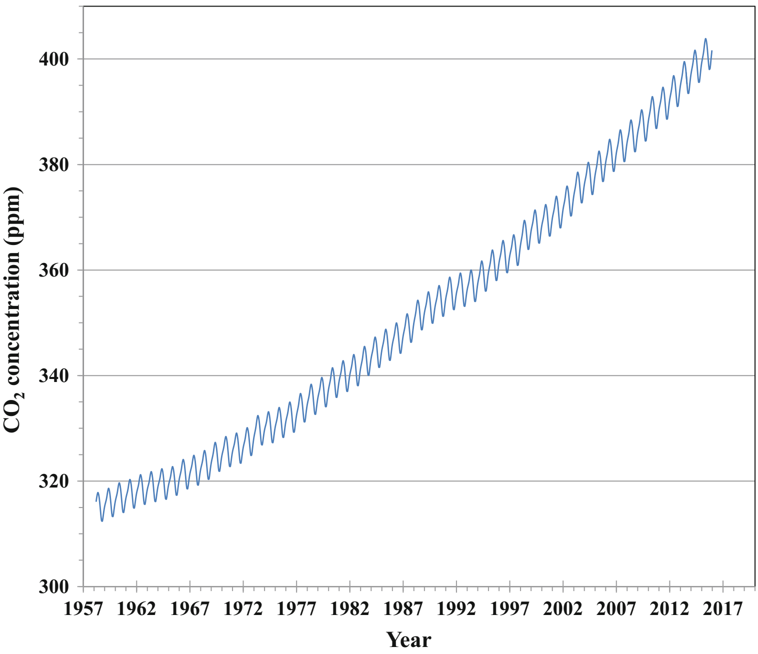

Fig. 6.2 Concentration of CO$_2$ in the atmosphere from 1958 to 2014 showing the effects of photosynthesis and the ecosystem respiration based on Mauna Loa station. *Data source* Keeling et al. (2016)

could be restored through reforestation and land management change, this would reduce the atmospheric CO$_2$ at the end of century by 40–70 ppm (Mackey et al. 2013). Complete reforestation of previously cleared land is impossible scenario however, due to competing land uses, especially food production and the need to feed an increasing human population. Conversely, complete global deforestation over the same timeframe would increase atmospheric CO$_2$ concentration by 130–290 ppm (House et al. 2002).

Photosynthesis and respiration processes are not evenly distributed in space or over the course of the year. About half of the photosynthesis occurs in the tropical regions where the conditions are generally favorable for growth and where a large proportion of Earth's land exists. The importance of terrestrial metabolism (i.e., photosynthesis and respiration) can be detected in the effect it has on the atmospheric CO$_2$ concentration (Fig. 6.2). The regular oscillations (Keeling cycle), which repeat annually are caused by metabolism of terrestrial ecosystem. The highest concentration occurs at the end of each winter following the season in which respiration has exceeded photosynthesis, thereby causing a net release of CO$_2$ to the atmosphere, while the lowest concentration occur at the end of each summer, following the season in which photosynthesis exceeds respiration and draws CO$_2$ out of the atmosphere. The longitudinal variability of these oscillations suggests that it is largely driven by northern hemisphere temperate and boreal ecosystems. The phase of the amplitude is reversed in the southern hemisphere corresponding to seasonal terrestrial metabolism of the southern hemisphere. Equatorial regions are thought to have less effect in these oscillations, despite high rates of production and respiration in this region. Seasonal changes in moisture in tropics affects both photosynthesis and respiration, and therefore, the two processes remain largely in phase with little or no net flux of CO_2 to the atmosphere.

6.2.2.2 Oceans-Atmosphere Natural Carbon Fluxes

The exchange of CO_2 between the atmosphere and oceans is a critical process of the global C cycling and an important determinant of the future of the Earth system (Fung et al. 2005; Friedlingstein et al. 2006). The global oceans determine the atmospheric CO_2 concentration in the timescales of millennia, and not vice versa, because DIC concentration in the oceans is 50 times that of the atmosphere (Falkowski et al. 2000). Over several thousands of years, the ocean CO_3^{2-} mineral saturation state is controlled by the balance of CO_3^{2-} mineral weathering on continents and subsequent input to the oceans, and CO_3^{2-} burial in ocean sediments (Ridgwell and Schmidt 2010). This balance helps establish fairly constant atmospheric CO_2 concentrations and ocean CO_3^{2-} chemistry on timescales >10,000 years. On the millennia timescales, the most important processes determining the exchanges of C between the oceans and the atmosphere are chemical equilibrium of dissolved CO_2, HCO_3^- and CO_3^{2-} in the ocean waters. The solubility and biological pumps acts in short-term to modify the long-term C equilibrium and keep the atmospheric CO_2 lower than otherwise it would be. Together, the two mechanisms keep DIC concentration of the surface waters about 10% lower than at the deeper depths.

The short-term exchange of C between ocean and atmosphere results from diffusion of CO_2 across the air-surface water interface. The pre-industrial era natural atmospheric CO_2 flux between the ocean and the atmosphere is estimated at 60–70 Pg C yr^{-1} in each direction (Sundquist et al. 2009; Ciais et al. 2013), which led to rapid equilibration of the atmosphere with the ocean surface waters. The capacity of oceans to buffer CO_2 concentration is finite and depends on the addition of cations from slow weathering of rocks. The rate of anthropogenic CO_2 emissions is several orders of magnitude greater than the supply of cations from mineral weathering on timescales of millennia. The ability of surface oceans to absorb CO_2 will therefore decrease as the atmospheric CO_2 concentration increases (Kleypas et al. 1999; Langdon et al. 2000; Andersson et al. 2013).

In the oceans, the CO_2 needed for photosynthesis is supplied from the atmosphere in dissolved form by the exchange with air at the ocean surface. Marine plants are the base of the oceanic food chain which eventually return respired CO_2

to the ocean surface and atmosphere. The annual rate of photosynthesis in the marine ecosystems is estimated at 45–50 Pg C yr^{-1} (Longhurst et al. 1995; Field et al. 1998; Fig. 6.1). About 25% of the primary production in oceans sinks from the photic zone to deeper waters (Falkowski et al. 1998; Laws et al. 2000). The gross flows of C between the surface ocean and the intermediate and deep ocean is estimated at about 40 Pg C yr^{-1}, part of this is from the sinking OM (11 Pg C yr^{-1}) and the other part is from physical mixing (33 Pg C yr^{-1}).

The net exchange of CO_2 across the air-sea interface varies longitudinally, mostly as a function of partial pressure of CO_2 in surface waters. The partial pressure of CO_2 in the surface waters is affected by water temperature, upwelling, or down-welling and biological production. Cold high latitude waters takes up CO_2, while warm lower latitude waters tend to release CO_2 (outgassing of CO_2 from tropical gyres). Even though the latitudinal pattern in net exchange is consistent with temperature, the most important reason for the exchange of CO_2 is upwelling in the tropics and down-welling or deep water formation at high latitudes. Under certain conditions, C buried in soils or marine sediments may not be back to the atmosphere and oceans for millions of years. These deposits of C comprise limestone and organic rock formation—including coal, oil, and natural gas deposits that are naturally recycled slowly through Earth's interior by geologic processes. Exposure to weathering ultimately returns rock C to the atmosphere and oceans.

6.2.2.3 Land-Ocean Natural Carbon Fluxes

Most of C taken up or lost by terrestrial ecosystems and oceans is exchanged with atmosphere. The C is also transferred through the aquatic continuum laterally across ecosystems and regional geographic boundaries, and also exchanged vertically with the atmosphere in the river channels, often as GHG. Prior to industrial revolution C export through rivers to ocean were almost balanced by loss of C to CO_3^{2-} sediments and release of CO_2 to the atmosphere. The lateral transport of C from land to sea has long been regarded as a natural loop in the global C cycle. However, recently, the anthropogenic perturbation of this loop is becoming apparent (Cole et al. 2007). The riverine export of DIC from fixation of atmospheric C resulting from rock weathering is estimated at 0.2–0.3 Pg C yr^{-1} (Suchet and Probst 1995). The rivers input of DIC to oceans estimated at 0.45 ± 0.18 Pg C yr^{-1} (Jacobson et al. 2007a) is almost balanced in a steady state by loss of C to CO_3^{2-} sediments estimated at 0.2 Pg C yr^{-1} and release of CO_2 to the atmosphere estimated at 0.1 Pg C yr^{-1} (Sarmiento and Sundquist 1992). Consequently, the level of atmospheric CO_2 varied by >25 ppm in the 10,000 years prior to 1850 (Joos and Prentice 2004). The riverine flux of OC is estimated at 0.2–0.5 Pg C yr^{-1} making a total C flux from land to the oceans range between 0.4 and 0.7 Pg C yr^{-1}.

6.3 Anthropogenic Perturbations to the Global Carbon Cycle

In the past three centuries, human perturbations of the environment have affected the biogeochemical behavior of the global C cycle through the additional burden of CO_2 added to the atmosphere by human activities. The human effects began thousands of years ago with conversion of forest and grasslands to agricultural land use, releasing CO_2 and possibly CH_4 to the atmosphere (Ruddiman 2005) and reached levels severe enough to outweigh natural change by the onset of industrialization in 1750. The pace of these effects accelerated in recent centuries with growing human population (Houghton et al. 1983; DeFries et al. 1999). The anthropogenic CO_2 emissions consist of two major fractions: (i) the CO_2 from fossil fuel, cement production, and gas flaring stored in geologic formation hundreds of millions of years, and (ii) the CO_2 emission from land use and land use intensity, i.e., deforestation, agricultural development and land use change, which have been stored for decades to centuries (Fig. 6.1). While emissions from fossil fuel combustion started before the Industrial Era, they only became the dominant source of anthropogenic CO_2 emissions to the atmosphere from around 1920s, and their relative share continued to increase until present. The emissions of CO_2 from burning of fossil fuel are currently the dominant anthropogenic CO_2 source.

The radiative properties of the atmosphere are strongly influenced by the abundance of well-mixed GHGs. Over the last two centuries, the anthropogenic activities—especially fossil fuel combustion and forest clearing have increased the emissions of CO_2, resulting into alteration of the global C cycle in important ways. The CO_2 is the gaseous phase of the global biogeochemical cycle of C which controls the complex flows of C between different components of Earth system, namely atmosphere, ocean, land, and lithosphere. The anthropogenic activities have specifically led to a rapid and dramatic increase in the concentration of CO_2 in the atmosphere and change the balance of the Earth's radiation (Hansen et al. 2005), while causing warming observed over the recent past (Hegerl et al. 2007). Since the beginning of the Industrial Era in 1750, the atmospheric CO_2 burden has increased by 260 ± 5 Pg C (Le Quéré et al. 2015, 2016). Multiple evidences indicate that the increase in atmospheric CO_2 concentration is the result of anthropogenic emission of CO_2: (i) atmospheric O_2 concentration has decreased over the past two decades, and the regional changes in O_2 content are consistent with regional variations of fossil fuel burning. Burning of fossil fuels consumes O_2 to produce CO_2 and lower O_2 concentration in northern hemisphere compared to southern hemisphere is consistent with the burning of fossil fuels, (ii) depletion of $\delta^{13}C$ (stable C isotopes) and ^{14}C (radiocarbon isotope) in the atmospheric CO_2 as a result of addition of large quantities of fossil C with lower $^{13}C/^{12}C$ ratio than the atmospheric CO_2, and also fossil fuel CO_2 is devoid of radiocarbon isotopes. The declining trends in ^{14}C is as expected with addition of fossil fuels CO_2 devoid of ^{14}C (Levin et al. 2010), and (iii) The rate of emission from fossil fuels and land use change is almost exponential, similarly the rate of atmospheric CO_2 increase. Anthropogenic emissions occur on top of an active natural C cycle that circulates C between the atmosphere, ocean, and terrestrial biosphere reservoirs on timescales ranging from days to millennia, while geological reservoirs have longer timescales (Archer et al. 2009).

The other components of global C cycle have also been altered significantly. The rising atmospheric CO_2 concentration has induced disequilibrium in the exchange fluxes between the land and atmosphere and the ocean and the atmosphere, respectively. On the land, the increased atmospheric CO_2 concentration fosters increased photosynthesis through CO_2 fertilization (Sarmiento et al. 2010; Schimel et al. 2015). The stimulation of plant biomass accumulation by elevated CO_2 concentration increases ecosystem C storage. However, the uncertainty regarding the magnitude of this biomass fertilization is the large unknown terrestrial feedback to C cycle-climate system. Experiments have shown that most C_3 plants responds to elevated CO_2 concentrations with increased rates of growth. Despite the stimulative effects of CO_2 on photosynthesis and plant growth, it is not clear, however, that the effects will result in an increased storage of C in the global ecosystems. It has been observed that plants often acclimatize to higher concentrations of CO_2 so that their rates of photosynthesis returns to the rates observed before the CO_2 concentration was raised (Oren et al. 2001; Dawes et al. 2011; Zak et al. 2011), suggesting diminishing or lack of CO_2 fertilization effects in some ecosystems and some plant species.

Similarly, increased atmospheric CO_2 induces atmospheric CO_2 partial pressure that reduces a net air to ocean flux and therefore increased ocean CO_2 sink (Graven et al. 2012; DeVries 2014). The consequences of these changes is that only about 43 ± 15% of the CO_2 emitted to the atmosphere from fossil fuel combustion and land clearing has remained in the atmosphere (Sabine et al. 2004a; Le Quéré et al. 2016). It is estimated that the anthropogenic activities have received a subsidy of approximately 360 ± 160 Pg C, which has been sequestered or hidden from the atmosphere. The uptake of anthropogenic CO_2 by the oceans primarily is a response to increasing CO_2 in the atmosphere. It is limited mainly by the rate at which anthropogenic CO_2 is transported from surface waters into the deep ocean (Sarmiento et al. 1992; Graven et al. 2012). This unmanaged sequestration makes it critical for accurately understanding the global C cycle, and future changes in climate. Future increases in unmanaged C uptake could moderate the risks of climate change, while decrease or transitions from uptake to release could amplify the risks dramatically. Recent climate trends, including ocean warming, changes in ocean circulation, changes in marine ecosystems, and changes in biogeochemical cycles will have effects on both ocean anthropogenic CO_2 sink as well as natural air-sea CO_2 fluxes.

6.3.1 Carbon Dioxide Emissions

On a multi-decadal and century time frame, increasing growth of CO_2 emission in the atmosphere is attributed to an anthropogenic CO_2 emissions comprising fossil fuel burning, cement production, and land use change (Trudinger et al. 2005). Direct observations and geophysical and biogeochemical models prediction of atmospheric CO_2 have established the consequences of anthropogenic activities on global C cycle. During the Industrial Era, combustion of fossil fuels and land use change contributed to a sharp rise in atmospheric CO_2 (Keeling et al. 2005).

6.3.1.1 Emissions from Combustion of Fossil Fuels, Cement Production and Gas Flaring

Fossil fuels—coal, oil, and natural gas are the residual OM formed millions of years ago by green plants. The materials escaped oxidation, became buried in the Earth, and over time were transformed to a fossil form through diagenesis processes. The energy stored in the chemical bonds is released during combustion, a process similar to respiration. When fossil fuels are oxidized, the CO_2 released represent a net increase in amount of C in the active system. But respiration merely redistributes the active C among reservoirs without changing the amount in the active system. The amount of C stored in fossil fuels reserves is larger than any other reservoirs except the oceans. Prior to industrial revolution, this C resource was not a significant part of short-term C cycling. However, industrial revolution changed that.

Organic C buried in sediments as coal, oil, and natural gas over hundreds of millions of years is being consumed as a result of human activities and returned to the atmosphere as CO_2 on timescales of few centuries. The energy from burning of fossil fuels provides heat, electricity, transportation, and industrial power. Inventory of CO_2 emissions from burning of three major fossil fuels: solid fuels (e.g., coal) liquid fuels (e.g., petroleum) and gaseous fuels (e.g., natural gas) together with cement production and gas flaring are generally grouped together in CO_2 emission analysis and termed as fossil fuel CO_2 ($FFCO_2$). Flaring of natural gas occurs as a byproduct of petroleum and natural gas extraction and processing. The natural gas co-produced in oil fields is sometimes burned at the well head or vented in areas deemed non-hazardous to humans. Cement manufacturing is the process of converting $CaCO_3$ to lime, with CO_2 byproduct produced emitted to the atmosphere. Emissions from cement production are one of the largest non-fuel combustion industrial source of CO_2 to the atmosphere. Emissions from gas flaring and cement production add a small amount to the total fossil fuels emissions. Emissions from cement production have increased slightly over the last three centuries, while emissions from gas flaring peaked on 1978 and continued to decline (Fig. 6.3), possibly due to improved technology to control the emissions. The $FFCO_2$ is the dominant anthropogenic CO_2 emission source. The global $FFCO_2$ emissions are generally compiled from fossil fuel production data or national and regional fossil fuels consumption calculated from data determined from national energy consumption statistics and converted to emissions by fuel type and then compiled internationally (Marland and Rotty 1984; Andres et al. 2012, 2014). Estimated uncertainty for the annual global emissions are on the order of 1–10% (Andres et al. 2012, 2014). The uncertainty has been increasing in recent decades because of

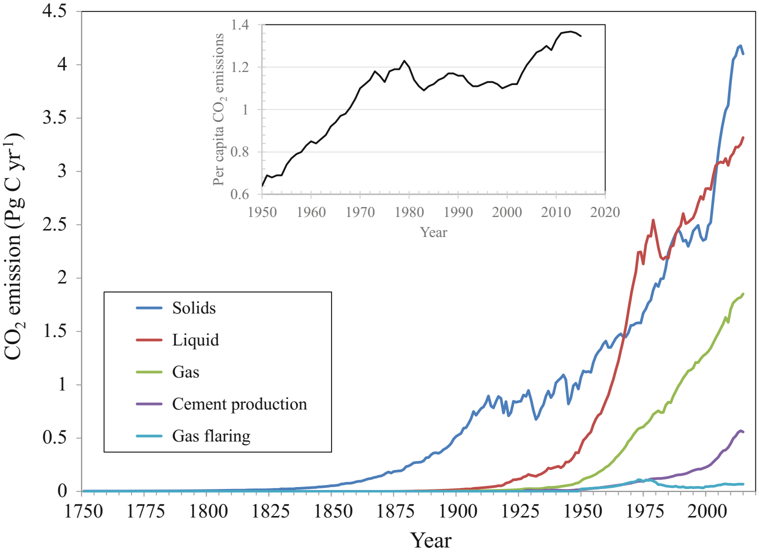

Fig. 6.3 The annual emissions of CO_2 from combustion of fossil fuels—coal, oil, and gas together with gas flaring and cement production from 1750 to 2013. *Data source* Boden et al. (2016). *Insert* shows per capita emissions from 1959 to 2015

larger fraction of the global emissions originating from emerging economies where energy statistics and emission factors per fuel type are more uncertain (Gregg et al. 2008; Andres et al. 2014). The uncertainty associated with production is less than that of consumption data, however, since fewer data points need to be collected for production, and these values are better known and easier to quantify.

Between 1751 (beginning of industrial era) and 2015, $FFCO_2$ have emitted 412 ± 20 Pg C to the atmosphere (Table 6.2) and projected to exceed 420 ± 20 Pg C in 2016 based on gross domestic production estimates (Le Quéré et al. 2015, 2016). Most of the $FFCO_2$ emissions occurred after 1850 (Fig. 6.3). The

Table 6.2 Fossil fuels and cement production carbon dioxide emissions (FFCO2) for 1751 to 2015 period. Data source: Boden et al. (2016), Le Quéré et al. (2015, 2016)

Sources	Emissions (Pg C)				
	1751–1850	1851–1958	1959–1990	1991–2015	1751–2015
Solids (coal)	1.3	62.0	56.2	75.2	194.7
Liquids (Oil)	0.0	11.8	60.4	72.7	145.0
Natural gas	0.0	2.5	18.9	35.7	57.1
Cement production	0.0	0.5	3.1	8.0	11.6
Gas flaring	0.0	0.3	2.2	1.3	3.8
Total	1.3	77.1	140.7	192.9	412.0

cumulative $FFCO_2$ emissions from 1751 to 1850 are estimated at 1.31 Pg C, and all of it originated from solids (coal) combustion. The $FFCO_2$ emissions from 1851 to 1958 are estimated at 77.1 Pg C, of which, coal, oil, and natural gas accounted for 50.5, 15.4, and 3.0%, respectively, with cement production and gas flaring accounting for <1%. The $FFCO_2$ emission from 1959 to 2015 is estimated at 334 Pg C, of which, coal, oil, natural gas, cement production and gas flaring accounted for 39.4, 40.0, 16.4, 3.3, and 1.05%, respectively.

The $FFCO_2$ emissions have increased every decade from an average of 3.1 ± 0.2 Pg C yr^{-1} in 1960s to an average of 9.3 ± 0.5 Pg C yr^{-1} during 2006–2015 decade (Table 6.3). Temporary interruption in the annual growth trends occurred during the two world wars (WWI and WW II), following the oil embargo and the associated increase in oil prices in 1973 and 1979, following the collapse of Soviet Union in 1992, and the global economic recession in 2008–2009 (Fig. 6.3; Friedlingstein et al. 2010, 2014). The 2015 emissions were distributed among coal (41.4%), oil (33.5%), natural gas (18.7%), cement production (5.6%), and gas flaring (0.7%), with emissions from coal, oil, natural gas, and cement production increased by 2.5, 0.7, 2.1, and 5.7% yr^{-1}, respectively during the 2006 to 2015 decade. The annual $FFCO_2$ for 2015 is projected at 9.9 ± 0.5 Pg C yr^{-1} (Table 6.3; Fig. 6.3). The growth rate in $FFCO_2$ showed decreasing trends between 1960s and 1990s from 4.5% yr^{-1} in the 1960s to 1.0% yr^{-1} in the 1990s before it began increasing again in the 2000s at an average rate ranging from 3.3 to 2.5% yr^{-1}. The global economic recession in 2008–2009 induced only a short-lived drop in CO_2 emission in 2009 of −0.3% with return to high annual growth rates of 5.1 and 3.0% in 2010 and 2011, respectively, and CO_2 emissions of 9.1 ± 0.8, 9.4 ± 0.8, 9.6 ± 0.5, and 9.9 ± 0.5 and 10.1 ± 0.6 Pg C yr^{-1} for 2010, 2011, 2012, 2013, and 2014, respectively. The growth in CO_2 emissions closely follows the growth in Gross Domestic Product (GDP) corrected for improvement in energy efficiency (Raupach et al. 2007). The growth rate in atmospheric CO_2 concentration in 2015 was 6.3 ± 0.2 Pg C, equivalent to 2.97 ± 0.09 ppm (Dlugokencky and Tans 2016).

The proportions of coal, oil, and natural gas production have changed through the time. Coal was the major CO_2 emission contributor until mid-1960s' when the CO_2 emissions from oil exceeded that of coal for the first time. The rates of oil and gas consumption grew rapidly until 1973, then their relative growth declined, and emissions CO_2–C from coal were nearly as large as those from oil during the second half of the 1980 and the last years of the twentieth century (Fig. 6.3). The increase in oil prices in 1973 following oil crisis forced the relative rates of growth to decline, such that emissions of CO_2 from coal were again nearly as large as those of oil during the second half of the 1980 s and in the last years of the 20th century. In 2009, the contributions from coal and oil were 40 and 35% respectively.

The relative contributions of different world regions and countries to the annual C emissions from fossil fuels have also changed over time. In 1925, the U.S., Western Europe, Japan, and Australia were responsible for 88% of the world's fossil fuel CO_2 emissions (Fig. 6.4). By 1950, the fraction contributed by these countries had decreased to 71% and by 1980 to 48%. The share of the world's $FFCO_2$ emitted by the developing countries has grown from 6% in 1925 to 10% in

Table 6.3 Decadal Global anthropogenic CO_2 emissions from fossil fuel combustion gas flaring and cement production ($FFCO_2$), land use and land cover change (LULCC), atmospheric CO_2 growth, compared with ocean and terrestrial sinks for 1960–2015

Source	1750–2015	1960–1969	1970–1979	1980–1989	1990–1999	2000–2009	2006–2015	2014	2015
Fossil fuels	410 ± 20	3.1 ± 0.2	4.7 ± 0.2	5.5 ± 0.3	6.3 ± 0.4	8.0 ± 0.4	9.3 ± 0.4	9.8 ± 0.4	9.9 ± 0.6
Land use change	190 ± 65	1.5 ± 0.5	1.3 ± 0.5	1.4 ± 0.5	1.6 ± 0.5	1.0 ± 0.5	1.0 ± 0.5	1.1 ± 0.5	1.3 ± 0.5
Atmospheric growth	260 ± 5	1.7 ± 0.1	2.8 ± 0.1	3.4 ± 0.1	3.1 ± 0.1	4.0 ± 0.1	4.5 ± 0.1	3.9 ± 0.2	6.3 ± 0.2
Ocean sink	175 ± 20	1.1 ± 0.5	1.5 ± 0.5	1.9 ± 0.5	2.2 ± 0.5	2.3 ± 0.5	2.6 ± 0.5	2.9 ± 0.5	3.0 ± 0.5
Terrestrial sink	165 ± 70	1.8 ± 0.7	1.8 ± 0.8	1.6 ± 0.8	2.6 ± 0.8	2.6 ± 0.8	3.1 ± 0.8	4.1 ± 0.9	1.9 ± 0.9

Data source Le Quéré et al. (2015, 2016)

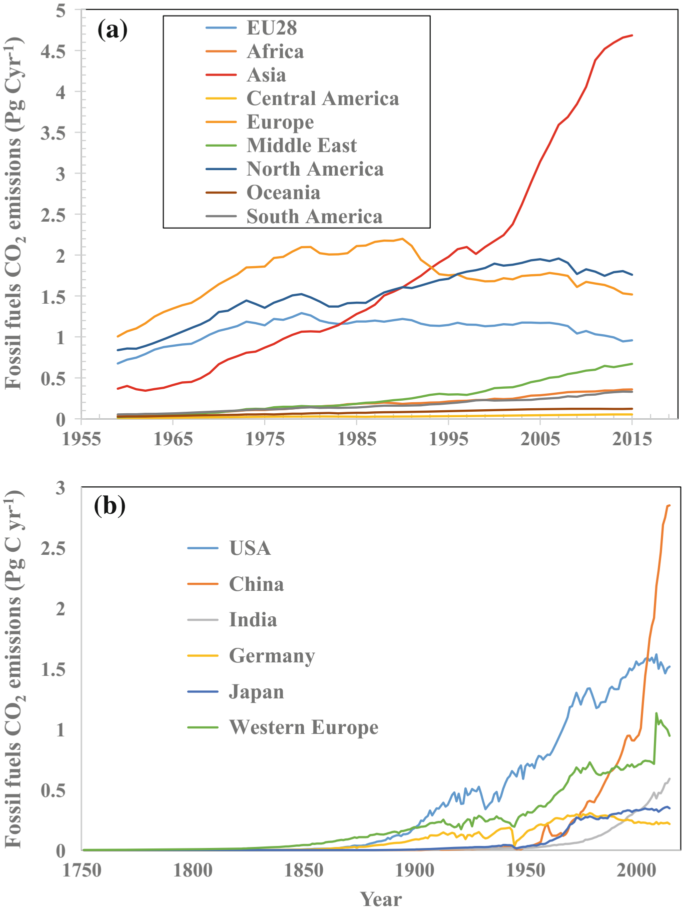

Fig. 6.4 Annual CO_2 emission from fossil fuel combustion, grouped based on **a** regional emissions and **b** territorial emissions for the top five emitters—USA, China, India, Japan, and Germany. *Data source* Boden et al. (2016)

1950, 20% in 1980. In 2006, $FFCO_2$ emissions from developing countries exceeded those from the developed countries. In 2009, developing countries contributed 57% of the $FFCO_2$ emissions. China passed the U.S. in $FFCO_2$ emissions in 2006 (Fig. 6.4). Most of the recent growth in $FFCO_2$ emissions has been from the developing countries. The annual rate of growth in the use of fossil fuels in the developed countries varied between 0.5 and 1.4% in 1970s, in contrast, the annual rate of growth in developing nations was 6.3% during this period. Between 2007 and 2009, China and India accounted for 92% of the growth in $FFCO_2$ emissions. In 2013, global emissions were dominated by China (28%), USA (14%), the European Union 28 member states (10%) and India (7%).

Although the annual emissions of CO_2 from fossil fuel combustion are small compared to natural flows of C through terrestrial photosynthesis and respiration (120 Pg C yr^{-1}) and relative to gross exchanges between oceans and atmosphere (90 Pg C yr^{-1}), however, these anthropogenic emissions are the major contributors to the increasing CO_2 concentrations in the atmosphere. They represent transfer of C from the slow geologic C cycle (old C) to the active C cycle.

6.3.1.2 Land Use Change

Evidence from archeology, environment history, and geological proxies suggest that human alteration of terrestrial ecosystems and the global natural C cycle began thousands of years ago with the conversion of forests and grasslands to agricultural land use and foraging in some regions, and possibly earlier with hunters and gatherers managing woodlands for hunting and traveling, at least since late Pleistocene with long-term impact from forest clearing and increased fire frequencies, resulting into mega faunal extinction, soil erosion and other land surface changes (Redman 1999; Kirch 2005). The disturbances associated with expansion of agriculture that started several thousand years before the industrial revolution has grown to create a human dominated world today (Pongratz et al. 2009). Despite the widespread recognition that hunter-gatherers and early farmers were capable of transforming the terrestrial ecosystems, these early anthropogenic changes have yet to be understood as global change processes, and are generally considered as localized and less significant compared to the contemporary changes in Earth system in the post-industrial revolution (Kirch 2005; Steffen et al. 2007). It is estimated that 30–50% of the Earth's land cover has been substantially modified by human land use, primarily the expansion of agriculture (Vitousek 1997; McGill 2015). There is a growing recognition that the anthropogenic land cover change has an impact on global climate, biodiversity, and the global C cycle, and need thorough investigation to understand its pathways of disturbance, its past, present, and future effects, as well as its potential role to mitigate CO_2 emission growth and climate change (Barker et al. 2007; Ciais et al. 2013; Smith et al. 2014; Blanco et al. 2014). Anthropogenic land use activities such as conversion of forest lands and grasslands to croplands and pasture, causes anthropogenic emissions of CO_2, mainly from biomass loss, decomposition of biomass and SOM, and by biomass combustion. Anthropogenic land use change accounts for about one third of anthropogenic CO_2 emissions from 1750 to 2011 and 12% of emissions in 2000–2011 (Houghton et al. 2012; Davis et al. 2014; Blanco et al. 2014). The land use change has reduced global transpiration by $\sim$10% while also increasing river discharge by 7% as identified by modeling study comparing present land use patterns to conditions under potential natural vegetation (Rost et al. 2008). The human appropriation of terrestrial NPP has been estimated at 24% of the total potential productivity (Haberl et al. 2007), which has doubled over the course of 20th century (Krausmann et al. 2013).

In addition to releasing CO_2 to the atmosphere, conversion of forests to cropland also modifies surface energy balance, evapotranspiration, surface roughness, and modifying surface albedo (Claussen et al. 2001; Betts 2000; Bonan 2008). Agriculture (i.e., domestication of crops and livestock) developed independently in several continents ~10,000 years BP near the onset of the Holocene to 5000 years BP: North America 10,000 years BP, South America 10,000 years BP, Near East 10,500 years BP, China 8000 years BP (Balter 2007). The agriculture had spread across most of Europe by 7700 years, reaching all if its arable regions by 5500 years ago (Zohary and Hopf 1993), while in China, irrigated rice was domesticated by 6500 years ago in Yangtze River Valley and adapted across China by 5000 years ago (Fuller et al. 2011). Ice cores records show the current interglacial period had CH_4 peak ~11,000 years BP which was followed by a steady decline in CH_4 concentration similar to previous interglacial periods. The CH_4 concentration begin to rise again at around ~5000 years BP, which has been attributed to onset of rice farming in Asia, a potent producer of CH_4. Likewise, CO_2 concentration was declining 11,000 years BP but then begin to rise ~8000 years BP, in contrast to previous interglacial periods in which atmospheric CO_2 continued to decline. The onset of farming together with domestication of ruminants may have released significant quantities of CO_2 and CH_4 into the atmosphere. These increases may have warmed the Earth sufficiently to avert a new ice age (Ruddiman 2003). The previous interglacial periods lasted on average ~10,000 years while in modern Holocene ~12,000 years have passed since the last ice age.

Despite the widespread recognition that hunter-gatherers and early farmers were capable of transforming terrestrial ecosystems, these medieval anthropogenic changes are generally considered as localized and less significant compared to contemporary changes in Earth system which have occurred since the onset of Industrial revolution in 1750 (Kirch 2005; Steffen et al. 2007; Pongratz et al. 2009). The global C cycle change has focused on the emergence of industrial processes over the last three centuries as the critical period within which global change processes, including increase in the rate of land use with growing human population became a significant forces driving global changes in the earth system (Kirch 2005; Steffen et al. 2011; Houghton et al. 1983; DeFries et al. 1999). Since 1750, anthropogenic land use change have resulted into 50 million km^2 being cleared for cropland and pasture, which correspond to 38% of ice-free land area (Foley et al. 2007, 2011) compared to the estimated area of 7.9–9 million km^2 under cropland and pasture in 1750 (Ramankutty and Foley 1999; Goldewijk 2001). A global land cover change derived from regional and global products by using remote sensing suggests that deforestation rate from all causes may be 1–5% yr^{-1} in active regions (Lepers et al. 2005). In addition, more than 85% of the global population increase to the current levels has occurred since 1850 (Ruddiman 2013). Therefore, the onset of the Industrial Era in 1750 marks a major inflection point in the human influences of the global environment.

6.3.1.3 Emissions from the Land Use Change

Substantial changes in atmospheric CO_2 concentration have been driven in part by human-induced land use change, and these changes will continue to occur in next century as the demand for ecological services from terrestrial environment continue to increase due to increasing global population. Three major drivers of changes in terrestrial C storage are (i) natural processes where C accumulation occurs in forests, wetlands, tundra, and prairies naturally, howbeit at generally low rates currently, (ii) direct human management activities such as deforestation and conversion of grasslands to cropland, pasture and urbanization, draining of wetlands, timber harvesting, and biomass burning, which have released much of C which had accumulated in these ecosystems over many centuries, and (iii) indirect effects of human activity such as increasing concentration of CO_2 in the atmosphere, increased rates of reactive N deposition, and changes in climate. These environmental factors may affect the rates of photosynthesis and respiration, potentially changing the C storage on land. The net effect of land use change and land management over millennia has been to reduce the amount of C stored in terrestrial ecosystems (Ellis 2011; Pinter et al. 2011).

Plants play a central role in the global C cycle through the uptake of CO_2 from the atmosphere. The terrestrial ecosystems have been C sinks in the past, and may still be sinks today where they exist (Luyssaert et al. 2008; Dommain et al. 2011; Donato et al. 2011). In addition, land management activities such as afforestation and vegetation regrowth on abandoned lands and restoration of degraded soils contribute to sequestering atmospheric CO_2 in wood products and soils (Houghton et al. 2012). Ideally change in land use would be defined broadly to include all forms of land management—a portion of terrestrial C that can qualify for credits under a post Kyoto agreement. However, it is impossible to separate management effects from indirect effects such as CO_2 fertilization, N deposition, or climate and other natural effects. Furthermore, the ideal land use change requires data at higher spatial and temporal resolution than currently possible and practical to assemble. Therefore, the dominant types of land use considered are (i) land use conversions, and (ii) land management practices. The activities associated with these types of land use changes and management forms the perspective of anthropogenic C sources and sinks considered under land use.

A critical distinction in estimating LULCC CO_2 emissions is estimate of gross and net CO_2 fluxes. Gross fluxes are individual fluxes from multiple processes involved in land use change that can be either emissions to the atmosphere or removal from the atmosphere at different timescales. The net flux of the land use change is the balance among all sources and sink processes involved in a given timeframe. Changes in the net terrestrial C balance occurs in two forms (i) net land use change emissions, which is the net change in terrestrial C pool (i.e., C release minus C uptake due to regrowth), and (ii) residual terrestrial C sink (i.e., the net effect of change in climate and CO_2 concentration). Changes in the amount of C held in global vegetation and soil are difficult to measure, and also more difficult to model because the land surface C content is not mixed, and also the background C levels is high and with greater spatial heterogeneity. Thus, initial estimates of global terrestrial C change were obtained by difference through the estimates of change in the other reservoirs—fossil fuels, atmosphere, and oceans. Because the global mass of C is conserved, when the three terms of C budget are known, the terrestrial C can be determined by difference (Houghton 2013).

The LULCC are generally associated with a reduction in vegetation (Baccini et al. 2012) and soil C storage, resulting in CO_2 emissions to the atmosphere (Houghton et al. 2012). The modification of land surface also affects biogeophysical properties such as albedo, surface roughness, soil moisture, and energy fluxes (Claussen et al. 2001; Bala et al. 2007) and biochemical properties including alteration of GHGs in response to changes in land-atmosphere fluxes of GHGs (Shevliakova et al. 2009). Albedo increases as a consequence of deforestation. It is estimated that 42–68% of the land surface has been affected by conversion to croplands and pastures and by wood harvesting since 1700 (Hurtt et al. 2006; Ellis 2011). The LULCC, often through the conversion of forests and grasslands to cropland is one of the principal mechanisms which human modifies the environment and climate. Deforestation and forest degradation contribute to atmospheric CO_2 emission through combustion of biomass and decomposition of remaining plant material and soil C. Deforestation is the long-term reduction of tree canopy cover to below 10–30%. In practice, deforestation is associated with the conversion of forest to other types of land use such as cropland or pasture (van der Werf et al. 2009). Conversion of forests to cropland does more than release of CO_2 to the atmosphere, it also modifies the near-surface energy balance, evapotranspiration, albedo, and surface roughness (Claussen et al. 2001). Changes in CO_2 occurs by both accelerated decomposition of OM and changes in biomass. Climate models and field studies have shown that in some regions (e.g., tropics, temperate, and boreal forests) modifying such biophysical parameters can impact climate more than the accompanying change in atmospheric CO_2 concentration (Betts 2000; Claussen et al. 2001; Bonan 2008). Changes in land use affect the amount of C stored in vegetation and soils, and hence, affect the flux of C between land and the atmosphere. Forest degradation is typically considered as partial deforestation, with more than 10–30% of forest cover remaining, for example, through selective logging (van der Werf et al. 2009). Land degradation that does not involve changes in tree cover density, such as oxidation and combustion of deforested and drained tropical peatlands may also involve substantial CO_2 emissions. The amount of C released to the atmosphere or accumulated on land depends on magnitude and type of changes in land use, and also the amounts of C held in different ecosystems.

Approaches to estimate global net fluxes from land use fall into three categories: (i) empirical book keeping models (Hall and Uhlig 1991; Houghton et al. 1983, 2012; Houghton 2003) that track C in living vegetation, dead plant material, wood products, and soils with cultivation, harvesting, and reforestation using country level reports on changes forest and biome-averaged biomass values, (ii) process-based terrestrial ecosystem models that simulate C pools in biomass and soil, and exchange fluxes between vegetation, soil, and atmosphere on a grid-basis (Shevliakova et al. 2009; Pitman et al. 2009; Pongratz et al. 2009; Olofsson and

Hickler 2008; Kato et al. 2013; Smith and Rothwell 2013), and (iii) detailed regional analyses based on satellite data that estimate changes in forest area or and biomass density (DeFries et al. 2002; Baccini et al. 2012; Harris et al. 2012). Satellite estimates of CO_2 emissions to the atmosphere from forest fires provides an additional constraint to this estimate (van der Werf et al. 2010).

The calculations using empirical book keeping method are based on rate of land use change and changes in C pools and stocks that follow a land use change (Houghton et al. 1983; Hall and Uhlig 1991). Changes in land use are broadly defined to include clearing of land for cultivation and pastures, the abandonment of agricultural lands, forest harvesting, reforestation, afforestation, and shifting cultivation. Some analyses have also included wild fires because of its effect on C storage (Houghton 1999). The C density (i.e., Mg C ha^{-1}) in vegetation and soils, and change in C density following the disturbance or management are specified from data reported in forestry and agricultural statistics and the ecological literature. Rates of land use change are generally obtained from agricultural and forestry statistics, historical accounts, and national handbooks. Carbon stocks and changes following disturbance and growth are obtained from field studies (Houghton 1999). For example, cultivation causes loss of 25–30% of C in the top 1 m soil depth (Post and Kwon 2000; Murty et al. 2002). Book-keeping approach assigns an average C density to all lands within a particular ecosystem type such as deciduous forest or grassland. It has large uncertainty, especially associated with deciding which ecosystems are converted to croplands and pastures, forests and non-forests. Even within forests, the spatial variability in C density is large, in part, due to variation in soils and microclimate, and in part, due to past disturbances and recovery. The bookkeeping empirical modeling does not yield annual net flux, because the processes considered and included in modeling are the ecological processes of disturbance and recovery (Houghton 2014). A modification of the approach uses remote sensing to map the aboveground biomass density. Recently, newer satellite-based techniques are currently being employed to determine and map aboveground carbon densities at higher resolutions (Goetz et al. 2009; Goetz and Dubayah 2011).

The second approach uses process-based terrestrial ecosystem models to estimate C density. The models also simulate spatial and temporal variations in ecosystem structure and physiology. Models differ with respect to details and the number of plant functional types and number of pools of C. The models have potential to simulate dynamics of biomass density by accounting for disturbances and recovery, both natural and anthropogenic (Cramer et al. 2001; McGuire et al. 2001). Maps are used to prescribe the anthropogenic land cover changes and the allocation of C to the atmosphere and to the soil. In the absence of historical maps, a specific criteria has to be applied to determine which land type has to be reduced or expanded (Pongratz et al. 2009). The limitation of the process-based modeling approach is lack of reliable historical maps, since the reliable satellite maps are only available from Landsat which began in 1972. In theory, Landsat data are available from 1972, but in practical terms, there are many holes in the coverage of Earth's surface until 1999 when the first global data acquisition strategy for moderate spatial resolution was undertaken with Landsat Enhanced Thematic Mapper Plus Sensor (Arvidson et al. 2001). Cloud cover and variations in phenology limit the ability to provide annual global updates of forest extent and change. The only other satellite system providing global coverage of land surface with annual update is the Advanced Land Observing Satellite (ALOS) Phased Array L-band Synthetic Aperture Radar (PALSAR) instrument (Rosenqvist et al. 2007). However, global mapping of change in forest cover based on ALOS-PALSAR data has not yet been operationally implemented. Bottom-up studies using dynamic global vegetation mechanistic models (DGMVs) represent many of the key land processes, and can be used to investigate how changes in structure and functioning of land ecosystems in response to environmental conditions affect biogeochemical cycles.

A portion of terrestrial sources of C can be determined from large changes in vegetation and soil C that result from changes in land use, including conversion of forest cleared lands. Changes in the use of land affects the amount of C stored in vegetation and soils. It also affects the fluxes of C between land and the atmosphere. The amount of C released to the atmosphere or accumulated on land depends on the magnitude and types of changes in land and also the amount of C held in different ecosystems. Conversion of grassland to pasture may result in no changes in C stock and therefore release no C to the atmosphere. In contrast, conversion of forest to agriculture will result in net loss of C stock and release C to the atmosphere as a result of increased mineralization of SOC. The primary emissions from land use are composed of two parts: (i) direct instantaneous release of C to the atmosphere from the vegetation biomass during land conversion process, which include respiration of plant products in short-term human use, e.g., domestic fuel, (ii) indirect emissions from decrease in NEP (Pongratz et al. 2009).

The net flux of CO_2 from changes in land use is important in the global C cycle since (i) changes in land use has caused a net release of C to the atmosphere over the last few centuries. However, the estimates vary, and the annual net release is more uncertain than other annual C budget (Le Quéré et al. 2009, 2015), (ii) estimates of net C from LULCC are important in determining whether air borne C fraction is changing. Air borne fraction is defined as the annual growth in the atmospheric CO_2 divided by the total annual emission—both fossil fuel and land use CO_2 emission.

Estimates of the amount of terrestrial C loss before 1850 are based on combination of three sets of data (i) estimate of natural vegetation cover (ii) the associated C densities in vegetation and soil, and (iii) the conversion of the natural covers to croplands and pastures based on a combination of agricultural maps and population density (Houghton 2014). Based on book keeping approach and process based dynamic terrestrial ecosystem models, the estimated land use CO_2 emissions before 1850 range from 18 to 114 Pg C (Table 6.4; DeFries et al. 1999; Olofsson and Hickler 2008; Pongratz et al. 2009; Van Minnen et al. 2009; Strassmann et al. 2008; Smith and Rothwell 2013). From 1850, the book keeping and process based models driven by land use show an emissions ranging from 108 to 210 Pg C (Table 6.4).

Annual net emissions from LULCC exceeded $FFCO_2$ prior to 1910, after 1950, $FFCO_2$ predominated (Fig. 6.5), even though both emissions accelerated with the

Table 6.4 The estimated net loss of C from global land use changes and land management

Reference	Approach	Total emission (Pg C)		Net emission ($Pg\ C\ yr^{-1}$)
		Losses before 1850	Losses from 1850	(2000–2010)
DeFries et al. (1999)	Book keeping model	48–57	182–199	0.90
Houghton (2003, 2010)	Book keeping model	–	155	1.50
Pongratz et al. (2009)	Process based model	53–63	108	1.14–1.13
Olofsson and Hickler (2008)	Process based model	79–114 (from 4000 BC)	148	–
Strassmann et al. (2008)	Process based model	45 (until 1700)	188	0.75
Shevliakova et al. (2009)	Process based model	–	164–188	1.07
Van Minnen et al. (2009)	Process based model	18	123	1.33
Houghton et al. (2012)	Book keeping model	–	100–200	1.14 ± 0.18
Smith and Rothwell (2013)	Process based model	41	210	0.8
Range	Book keeping	48–57	155–200	0.90–1.50
	Models	18–114	108–210	0.75–1.33

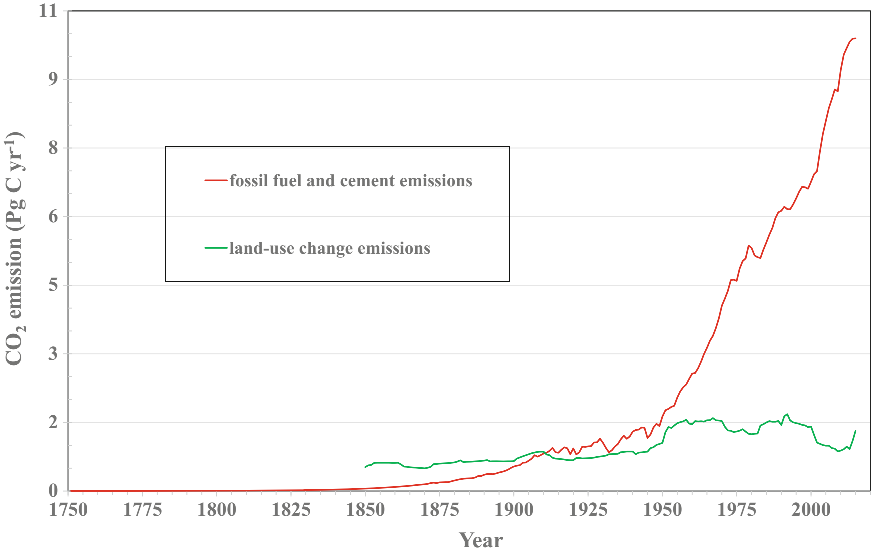

Fig. 6.5 Global emissions from fossil fuels combustion and land use and land use change. *Data source* fossil fuel emission: Boden et al. (2016), land use emissions: Le Quéré et al. (2015, 2016)

intensification of industrial activity and expansion of agriculture area as a result of population increase. Estimated land use emissions from 1850 to 1958 were 82.4 Pg C or 52% of total C emissions. However, from 1959 to 2013, land use emissions were 19% of total C emissions (Fig. 6.5, Gibbs and Herold 2007; Schrope 2009). In the 2004–2013 decade, land use change, including deforestation forest degradation and decomposition of soil C emissions accounted for 10% (range 6–17%) of total anthropogenic emission of C (van der Werf et al. 2009). The declining fraction is largely the result of rise in fossil fuel emissions. Based on book keeping and dynamic global vegetation models, the decadal CO_2 emission in 1960s, 1970s, 1980s, 1990s, and 2000s were 1.3 ± 0.5, 1.2 ± 0.6, 1.3 ± 0.6, 1.8 ± 0.9, and 1.1 ± 0.7 Pg C yr^{-1}, respectively (van der Werf et al. 2009; Friedlingstein et al. 2010; Le Quéré et al. 2015). The lower estimates in 2000–2009 compared to 1990s are primarily due to lower rates of deforestation in tropical Asia and Brazilian Amazon detected from satellite data (Regalado 2010; Hansen et al. 2009). Temperate forest regrowth in Eurasia has constantly increased since the 1950s at a rate of 0.2 Pg C yr^{-1} per decade (Friedlingstein et al. 2010). The data suggests that the CO_2 emission rate from LULCC have generally remained constant at around 1.4 ± 0.5 Pg C yr^{-1} between 1960 and 1999, and decreased to 1.0 ± 0.5 Pg yr^{-1} for the last decade (2006–2015) (Le Quéré et al. 2015, 2016). However, the annual net release is more uncertain than other terms in the global C cycle budget (Le Quéré et al. 2009). Most of the C emissions from LULCC in recent years (post 1950) have from the tropical regions globally.

Emissions from the LULCC amounted 156 Pg C or 36% of all anthropogenic CO_2 emissions between 1850 and 2000 (Houghton 2003; Pongratz et al. 2008) and 1.1 ± 0.7 Pg C yr^{-1} during the first decade of the 21st century, although their share of the total emissions has declined significantly due to the increasing contribution of fossil fuels (Friedlingstein et al. 2010). Over the 1751–2015 period, cumulative net CO_2 emissions from land use, land management, and land use change of 190 ± 70 Pg C has been estimated (Ciais et al. 2013; Le Quéré et al. 2015, 2016). The C losses LULCC from 1850 represent 65–73% of all time losses from LULCC (Table 6.4). About 90% of this more recent loss is estimated to be the result of clearing and management of forests, while cultivation of prairie soils contribute to the remaining 10% (Pongratz et al. 2008). Deforestation had the greatest effect on emissions from the LULCC, accounting for 110 Pg C. In addition, widespread harvest of wood and other processes have contributed 40 Pg C or 25%.

The temporal variations in the terrestrial C sources and sinks can also be determined through inverse calculation with ocean C models (Gruber et al. 2009; Khatiwala et al. 2009; Le Quéré et al. 2010) that calculate the annual sources and sinks of C necessary to produce observed concentrations of CO_2 in the atmosphere and oceans, and then subtracting the known $FFCO_2$ emissions from calculated sources and sinks which yields a residual flux of C, assumed to be terrestrial C flux, because the other terms have been accounted for. Atmospheric CO_2 based top-down approaches provide large scale constraints on the land and ocean surface processes, but they cannot identify processes or regions driving the observed changes unambiguously (Sitch et al. 2015).

Although, the LULCC CO_2 emissions are important in the global C cycle, the quantitative understanding of these emissions estimates remain highly uncertain compared the other fluxes, however. Changes in land use not only affect CO_2 emissions to the atmosphere, they are also important for C management and policy. Protection of land to minimize future emissions of CO_2 by deforestation or other land use changes has gained wide international support (Gullison et al. 2007; Turner et al. 2009). Economists also argue that C sequestration in agricultural lands and reductions of emission from LULCC and deforestation can be some of the most cost effective approaches to GHG control (Stern et al. 2006; Eliasch 2008). It is estimated that the degradation of forests has reduced the C density of forest biomass from global average of ~100 Mg ha^{-1} in pre-disturbance to current ~90 Mg ha^{-1} (Houghton et al. 2012). The rate of the land use change has been accelerating globally, albeit with different extent in different regions. In USA and Europe, and largely developed countries, the agricultural land area has remained nearly constant over the last few decades, while in the tropical regions the agricultural lands have been expanding at the expense of forest land and grassland.

6.3.1.4 Increase in Atmospheric Carbon Dioxide

Measurement of gas concentration in the bubbles of air trapped in glacial ice made it possible to constrain atmospheric gases reliably. However, there were no reliable measure of the annual rate of increase in atmospheric CO_2 concentration until after 1957 when the first continuous monitoring of the atmospheric CO_2 were initiated by C.D. Keeling from Scripps Institution of Oceanography at Mauna Loa, Hawaii and at the South Pole (Keeling et al. 1976). In 1958, the atmospheric CO_2 concentration had reached 315.7 ppm (Keeling et al. 1976), suggesting a 12.5% increase between 1750 and 1958. Soon after the first high precision measurements of atmospheric CO_2 started, it became clear that the global mean CO_2 growth rate is substantially lower than expected if all anthropogenic CO_2 emissions remained in the atmosphere (Keeling et al. 1976). The search for this 'missing' C and the identification of the processes driving the sinks has dominated C cycle research for the past three decades (Tans et al. 1990; Sarmiento and Gruber 2002; Gruber et al. 2009). Much progress has been achieved (Le Quéré et al. 2009; Khatiwala et al. 2013; Wanninkhof et al. 2013), but spatial attribution of recent sink rates, and for oceans and land and their changes over time remains uncertain (Le Quéré et al. 2015; Sitch et al. 2015).

Currently there are nearly 200 stations worldwide where samples of air are collected and analyzed for CO_2 and other atmospheric constituents, resulting into integrated global datasets. The globally averaged atmospheric CO_2 concentration reached 400.0 ± 0.1 ppm at Mauna Loa in July 2014, and the global average CO_2 concentration in 2015 were 400.0 ± 0.1 ppm, which constitutes a relative abundance of 144% relative to pre-industrial levels in 1750 (WMO 2016), corresponding to an increase in CO_2 atmospheric burden of 260 ± 5 Pg C (Le Quéré et al. 2015, 2016). Over the eight glacial cycles, the CO_2 concentration varied from about 180 ppm during glacial periods to about 280 ppm during interglacial periods, and the correlation between CO_2 concentration and global surface temperature is evidence for greenhouse effect of CO_2 first advanced about a century ago by Swedish climatologist (Arrhenius 1896). Over the last 1000 years before the industrial revolution the atmospheric CO_2 concentration varied by <10 ppm. The

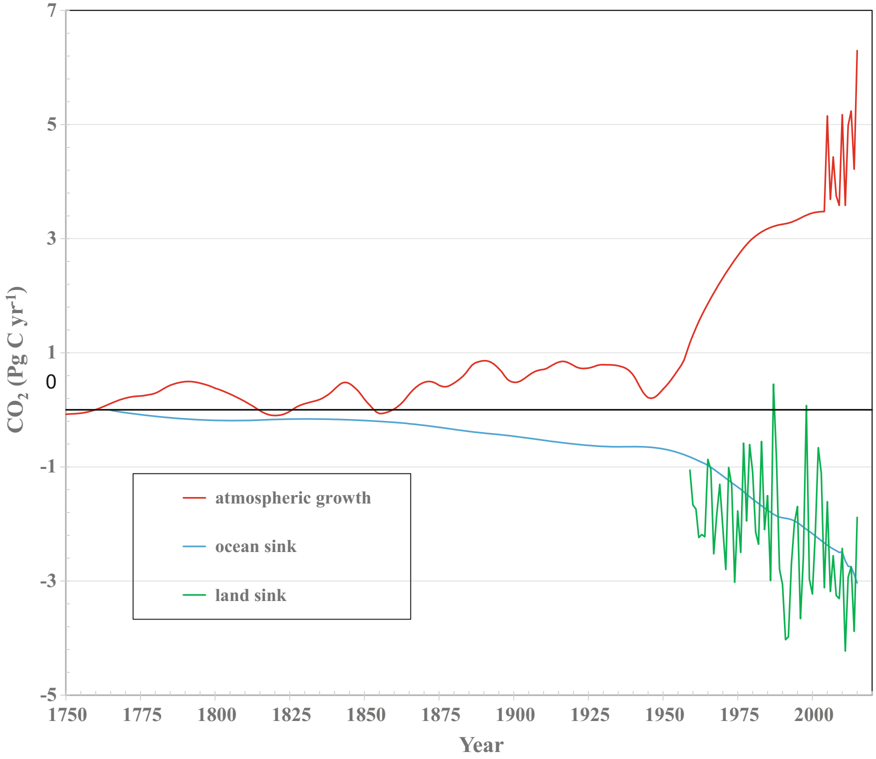

Fig. 6.6 Atmospheric CO_2 growth compared to ocean and terrestrial CO_2 sinks. *Data source* Le Quéré et al. (2015, 2016), Dlugokencky and Tans (2016)

data from ice core from Vostok Antarctica and Dome Fuji demonstrate that the atmospheric CO_2 concentration is currently higher than at any time during the past 800,000 years (Petit et al. 1999; Kawamura et al. 2003).

The growth in atmospheric CO_2 for the early period of 1750–1850 was about 20.4 Pg C, and from 1851 to 1958 was about 59 Pg C. Cumulative atmospheric CO_2 growth from 1750 to 2014 is 256 ± 5 Pg C (Table 6.3). The data generally show seasonal variability but year to year increase in concentration during the Industrial Era (Fig. 6.6). The most conspicuous is the interval from about 1944 to 1955 which atmospheric CO_2 concentration stabilized (Trudinger et al. 2002), possibly caused by slightly decreasing temperatures over land in the northern hemisphere (Rafelski et al. 2009). The decadal average rate of increase was 1.0 ppm yr^{-1} in 1950s and 1960s, and increased to about 1.5 ppm yr^{-1} in the 1980s and 1990s, and 1.9 ppm yr^{-1} between 2000 and 2010. The decadal atmospheric CO_2 growth rate increased from 1.7 Pg C yr^{-1} in 1960s to 4.3 ± 0.1 Pg C yr^{-1} during 2004–2013 with some important decadal variation (Le Quéré et al. 2015; Table 6.3). The atmospheric increase above the preindustrial concentrations was initially caused by the release of C from deforestation, land use conversion and agricultural land use (i.e., anthropogenic land uses emissions; Fig. 6.5). Although the emissions of fossil fuel combustion started before industrial era, they only became the dominant source of anthropogenic emissions to the atmosphere from around 1920, and then the relative share continued to increase until present. The atmospheric C content represents the balance between anthropogenic C emissions and natural sources and sinks. In the absence of anthropogenic emissions, sources and sinks are approximately balanced over multi-decadal timescales, and atmospheric C content would therefore remain relatively constant over these timescales.

Anthropogenic induced emissions of CO_2 have increased substantially at accelerating rate over the two centuries since the onset of Industrial revolution. This increase has been the principal driver of the observed increase in global temperature since 1970s when the temperature signal began to emerge from the noise associated with natural temperature variations. The increase in CO_2 emissions from fossil fuel burning and those arising from land use change are the dominant cause for the observed increase in atmospheric CO_2 concentration. Four lines of evidence support this conclusion:

(i) Known sources of C (i.e., fossil fuel burning and land use emissions) are more than adequate to explain the observed CO_2 increase in the atmosphere. Balancing the global C budget requires unaccounted sink of C and not unexplained source of C. For example, between 1750 and 2013, fossil fuel burning released 395 ± 20 Pg C, and additional 185 ± 65 Pg C was released from LULCC emissions. The observed increase in atmospheric CO_2 over this period was only 250 ± 5 Pg C (Table 6.3).

(ii) Pre-industrial Era CO_2 concentration varied by ~ 10 ppm for several thousand years. Between 1750 and 2014, the atmospheric CO_2 concentration increased by 121 ppm (about 44%). The timing of this increase coincides with CO_2 emissions from fossil fuel burning and the net emissions from land use change.

(iii) The latitudinal gradient in the CO_2 emission is the highest at northern and mid-latitudes and lower at higher and lower latitudes, consistent with increased emissions from fossil fuel burning located in northern and mid-latitudes, although atmospheric transport of CO_2 is rapid, this signal can be detected.

(iv) The rate of increase of atmospheric C and the distribution of C isotopes ($^{13}C/^{12}C$) and radiocarbon (^{14}C) and other biogeochemical tracers (including decrease in atmospheric O_2 concentration) are consistent with the scientific understanding of the anthropogenic C sources from fossil fuels and land use and C sinks the ocean and terrestrial uptake. For example, the ^{14}C content of the atmospheric CO_2 has decreased with increase in fossil fuel C (dead C) in the atmosphere.

The annual atmospheric CO_2 increase accounts for only about 40–45% of the anthropogenic CO_2 emissions produced annually by fossil fuel burning, deforestation and land use change, and soil degradation (Canadell et al. 2007b). The remainder of the CO_2 is being removed from the atmosphere by the response of the natural C cycle. Anthropogenic CO_2 is being dissolved in oceans, and some is being taken up by the terrestrial vegetation. Some of the findings points toward the likelihood of large forest sinks in the northern temperate latitudes (Tans et al. 1990; Caspersen et al. 2000). Other studies suggest a possibility of significant terrestrial uptake in the tropics (Jacobson et al. 2007b; Stephens et al. 2007). It is estimated that global oceans are taking 30%, while terrestrial biosphere is taking 20% (Sabine et al. 2004c). It is now well established that surface ocean pCO_2 may be as three times their industrial values near the end of this century. There are indications that the fraction of oceans uptake may be decreasing, and natural sinks may not be able to keep pace with the increase in fossil emissions due to ocean acidification (i.e., surface pH decrease), and also some portion of terrestrial biosphere is reaching saturation (Canadell et al. 2007b).

Recent studies have emphasized the potential importance of climate—CO_2 feedback mechanisms that may be critical to understanding both the C cycle's sensitivity to climate (Fung et al. 2005; Friedlingstein et al. 2006; Cox and Jones 2008). Overall, the changing C cycle is viewed not only as the primary driver of climate change but as a primary source of uncertainty in projecting future climate trends. Boreal forests and northern peat lands which accounts for large global terrestrial C storage already experiencing significant warming—resulting in large scale permafrost thawing and dynamics changes in aquatic and forest ecosystems (Ise et al. 2008; Schuur et al. 2008). The warming makes stored C under boreal and permafrost vulnerable to decomposition, with potential of releasing large quantities of CO_2 to the atmosphere. Forests and woodlands may also become susceptible to C loss caused by climatic change (Breshears et al. 2005; van Mantgem et al. 2009).

6.3.2 Anthropogenic Fluxes of Carbon

During the past two centuries human activities have greatly modified the exchange of C between land, atmosphere, fresh water bodies, coastal zones, and open oceans (Mulholland and Elwood 1982; Stallard 1998; Ver et al. 1999; Raymond et al. 2008). The partitioning of the anthropogenic CO_2 emissions from fossil fuel burning and land use activities between the sinks of atmosphere, ocean, and land has been of interest among scientists for the past three decades, and atmospheric and oceanic monitoring data and model simulations confirms the importance of these sinks (Le Quéré et al. 2009; Sitch et al. 2015). Between 1959 and 2013, an average of 44% of each year's CO_2 emissions remained in the atmosphere, the rest was absorbed by sinks on the land and in the ocean (Le Quéré et al. 2009, 2015). On average, the fraction that of CO_2 emissions that remains in the atmosphere has increased from about 40–45%, and the trend was caused by a decrease in the uptake of CO_2 by the C sinks, possibly in response to climate change and variability. However, changes in sinks are highly uncertain.

The atmosphere-land and atmosphere-ocean fluxes of CO_2 are known to be sensitive to climate. For example, the growth rate of atmospheric CO_2 varies with El Nino South Oscillations (Bousquet et al. 2000), and also believed to have been affected by the climate perturbation arising from Pinatubo volcanic eruption (Lucht et al. 2002). Projected changes in sea surface temperature and oceanic circulation lead to a reduction of C uptake (Sarmiento et al. 1998; Chuck et al. 2005). As the temperature of surface waters increases, their density decreases and they become more buoyant compared with deeper waters whose temperature remains largely unchanged, resulting into a decrease in mixing ratio due to stratification, and greater relative changes in pCO_2. Since the increase in CO_2 leads to climatic change, and climate change in turn affects CO_2 concentration, the climate, atmospheric CO_2, and the C cycle form a feedback loop.

6.3.2.1 Ocean—Atmosphere Exchange Fluxes

The global oceans play an important role in the global C cycle by mitigating the perturbation effects of the climate system resulting from the anthropogenic CO_2 emissions. The oceanic reservoir of C is about 50 times that of the atmosphere (Sabine et al. 2004c), therefore, even small changes in ocean C reservoir can have large impact on the atmospheric CO_2 concentrations. The ocean-atmosphere exchange of CO_2 occurs rapidly, as a result, ocean absorbs substantial portion of anthropogenic C from the atmosphere. The oceans have absorbed about a quarter to a third of anthropogenic CO_2 emissions over the industrial period and contributed to mitigation of large-scale effects of anthropogenic greenhouse effect by slowing the rate of climate change (Le Quéré et al. 2010; Khatiwala et al. 2013), and this will continue over the next century, based on carbon-climate models estimates (Friedlingstein et al. 2006), highlighting a crucial role of oceans as the ultimate sink for anthropogenic CO_2. With the net removal of anthropogenic CO_2 over the industrial period oceans constitute the only sink over the last 200 years, since terrestrial biosphere is most likely net source when integrated over the entire period (Sabine et al. 2004a). This has led to enhanced interest in understanding the cycling of CO_2 between the atmosphere and the ocean because the increase in increase in atmospheric CO_2 concentration increases the flux across the air-sea interface.

The absorption of anthropogenic CO_2 by the oceans involves several processes: (i) air-sea exchange of CO_2, driven by the difference in CO_2 partial pressure (pCO_2) between atmosphere and ocean surface waters; (ii) buffering between dissolved CO_2 and DIC (i.e., total inorganic C including CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}), only about 10% of C crossing the air-sea interface contributes to aqueous pCO_2, and the rest occurs as other forms of DIC without contributing to pCO_2; (iii) the ocean circulation pump which export C from surface to deep waters; and biological pumps which export soft tissue and CO_3^{2-} detritus from ocean biota in the surface waters to deep waters as they sink.

Because of the chemistry of seawater, the distribution of inorganic C is such that 98.5% of the C in the ocean-atmosphere system is in the ocean as DIC. However, most of it is in the form of HCO_3^- and CO_3^{2-}, and less than 1% is in the form of dissolved CO_2 (Table 6.3). The seawater CO_3^{2-} chemistry is governed by a series of chemical uptake of the atmospheric CO_2, dissolution, and precipitation reactions (Eqs. 6.4, 6.5), (Sabine and Tanhua 2010).

$$\text{Air-sea exchange: } CO_{2(g)} \leftrightarrow CO_{2(aq)} \tag{6.4}$$

$$\text{Reaction with water and precipitation: } CO_{2(\mathrm{aq})} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \tag{6.5}$$

These reactions are relatively rapid and for most applications the partitioning of DIC in water can be assumed to be in equilibrium. The equilibrium timescale for the air-sea CO_2 exchange is about 1 year. This equilibrium also sets up a buffer for changes in ocean C which is determined by reaction of CO_2 to produce HCO_3^- (Sarmiento and Gruber 2002). Therefore, on a global scale, surface water CO_2 generally increases at close to the same rate as the atmospheric CO_2 concentration (Takahashi et al. 2009), although local physical or biological perturbation events can make surface water CO_2 significantly deviate from the atmospheric equilibrium. For typical surface ocean conditions, the distribution of the DIC among HCO_3^-, CO_3^{2-}, and undissociated CO_2 (i.e., $CO_{2(aq)}$ and H_2CO_3) are 90, 9 and 1%, respectively (Sabine and Tanhua 2010).

The anthropogenic uptake of CO_2 by the ocean occurs on the top of very active natural oceanic C cycle and the contemporary exchange flux of CO_2 across the atmosphere-sea interface consists of a natural component and the anthropogenic CO_2 that is generally driven by anthropogenic perturbations of atmospheric CO_2. Both natural and anthropogenic C components are expected to change considerably in the future in response to continuously rising atmospheric CO_2 and global climate change (Sarmiento et al. 1998; Gruber et al. 2004; Yoshikawa et al. 2008). Ocean biology plays important part in the natural distribution of C in the ocean. But the uptake and storage of anthropogenic C is the chemical and physical response to the rising atmospheric CO_2 concentration. Therefore, the amount of DIC in the ocean determines the atmospheric CO_2 concentration in the long term due to large pool of inorganic C in the oceans. The net global uptake of atmospheric CO_2 plays major role in reducing atmospheric CO_2 and moderating the impact of the CO_2 emitted into the atmosphere.

Although the oceans determine the atmospheric CO_2 concentration in the long term, lags introduced by other processes beside water chemistry allow a temporary disequilibrium. The processes that delay the transfer of anthropogenic CO_2 into the ocean are (i) the transfer of CO_2 across the sea-air interface and (ii) the mixing of water masses within the sea. The transfer of CO_2 from the air to sea is believed to have reduced the oceanic absorption of CO_2 by about 10% (Broecker et al. 1979). The anthropogenic activities during the Industrial Era have increased ocean-atmosphere CO_2 fluxes. The net CO_2 flux from the atmosphere to the ocean has increased by 20 Pg C, while the net increase of the CO_2 flux from the ocean to the atmosphere has increased by 17.7 Pg C (Fig. 6.1). One of the important process which is slowing the ocean uptake of CO_2 is the rate of vertical mixing within the oceans. On timescales of decades, the rate at which anthropogenic C is moved into the ocean interior limits the rate of ocean uptake (Sarmiento and Sundquist 1992). The physical mixing time for the ocean is two to three orders of magnitude slower compared to the mixing time of the atmospheric CO_2, and it is the primary process controlling large-scale CO_2 uptake in the ocean (Stuiver et al. 1983). The CO_2 uptake at the surface does not fully explain the spatial differences in CO_2 storage in the ocean due to slow mixing time in the ocean interior, and the fact that surface waters only moves into the deep ocean in a few locations in the ocean (Sabine and Tanhua 2010). Currently the rate of ocean C storage does not seem to keep pace with the rate of growth in CO_2 emissions (Rhein et al. 2013). Over hundreds to thousands of years, however, the oceans will be absorb 70–80% of CO_2 released to the atmosphere (Archer et al. 1997).

Measurements of Ocean Uptake of Anthropogenic CO_2

The direct measurements of changes in the amount of C in the world's oceans and estimation of the storage of anthropogenic CO_2 in the ocean is difficult task because: (i) anthropogenic CO_2 in the ocean is not a directly measurable quantity, it has to be inferred using indirect means, (ii) the oceans are not mixed as rapidly as the atmosphere. As a result, the spatial and temporal heterogeneity is large, and (iii) the background concentration of dissolved C in sea water is large relative to the anthropogenic C change, so the measurement of the change requires very accurate methods.

A further complication is that C in the ocean participates in complex in situ biogeochemistry. The anthropogenic CO_2 of the ocean is superimposed on the natural oceanic C cycle, and measurements provides combined natural and anthropogenic CO_2 emission. The anthropogenic CO_2 flux primarily responds to the increase in atmospheric CO_2 with climate variability such as wind and ocean circulation having a minor impact (Lovenduski et al. 2008), while, the natural CO_2 fluxes are not impacted by the rise in atmospheric CO_2, but can change substantially in response to climate (Le Quéré et al. 2010).

Knowledge of exchanges of CO_2 with the atmosphere at the sea-air interface is important because the magnitude and direction of fluxes are indicative of biogeochemical C cycling in the ocean. Estimates of globally integrated sea-air C fluxes are relevant for quantifying the ocean uptake of anthropogenic CO_2 (Sabine and Tanhua 2010). Two approaches have been used to directly measure of anthropogenic C in the ocean (i) measurement of changes in the oceanic inventory of C (ii) measurement of the transfer of CO_2 across the air-sea interface. Direct measurement of an increase in ocean C is complicated by the background concentration and natural variability of C concentrations in sea water.

Model based calculations of the total uptake of anthropogenic CO_2 in the surface waters of the ocean are about 40 μmol CO_2 kg^{-1} of water. Therefore, the annual increase in DIC would be much smaller than 40 μmol CO_2 kg^{-1} as would be the increase in DIC concentrations in deeper waters, where less anthropogenic C has penetrated. By comparison, the background concentration of DIC in surface waters is 2000 μmol kg^{-1} (Sarmiento 1993). Even though the analytical techniques have very high precision, against this large background and also large variability, direct measurement of change in CO_2 concentration is a challenge (Sarmiento 1993). The spatial and temporal variability also makes the direct measurement of the sea-air CO_2 exchange fluxes difficult. Although analytical are capable of a precision of 1.5 μmol kg^{-1} (Sarmiento 1993), the uncertainties are high due to spatial and temporal variability.

The air-sea flux of CO_2 is calculated from the observed difference in pCO_2 across air-water interface, the solubility of CO_2 in sea water, and the gas transfer velocity (Wanninkhof et al. 2009). The approach measures the concentration of CO_2 in the air and in the ocean surface mixed layer. The difference defines the gradient which together with model that relates the exchange coefficient to wind speed enables the rate of CO_2 exchange to be calculated. An average air-sea difference of 8 ppm globally is equivalent to oceanic uptake of 2 Pg C yr^{-1} (Sarmiento 1993). Natural variability together with spatial and temporal variability make accurate estimates difficult. Furthermore, the gas transfer coefficient is also uncertain within the factor of 2 (Broecker 2001). Air-sea flux is driven by physical and biogeochemical processes that make accurate assessment of sea-air CO_2 flux challenging, and the available measured values have limited geographic and temporal coverage (Wanninkhof et al. 2013). Estimates of the net air-sea CO_2 flux based on measurements of pCO_2 in the near-surface seawater and in the marine boundary air show that the extratropics are the major oceanic sinks of atmospheric CO_2 and the tropics are the major sources.

Ocean Carbon Models

Because of these difficulties in measuring changes in inventories of C or the uptake of anthropogenic C across the air-sea surface directly, the uptake of anthropogenic C by the oceans is calculated by models that simulate the chemistry of CO_2 in seawater, the air-sea transfer of CO_2, and oceanic circulation or mixing of the ocean's water masses (Wanninkhof et al. 2009, 2013; Khatiwala et al. 2013). The models estimate the annual uptake of C by global oceans. The three tracers—CO_2, radioisotope of C ($^{14}CO_2$) and the penetration of CFCs into the ocean have been used to constrain the models (Gruber et al. 1996; Broecker et al. 1995; McNeil et al. 2003). The difference between current distribution of CO_2 in the ocean and that expected without the anthropogenic emissions yields estimate of oceanic uptake (Gruber et al. 1996). This approach is based on changes that occur in the chemistry of ocean water as it ages, including OM decay, decrease in O_2 concentration, and changes in alkalinity. Based on concentration of CO_2, O_2, and alkalinity throughout the ocean, it is possible to calculate the increased abundance of C in the ocean as a result of increase in atmospheric CO_2. The approach is based on the assumption that the surface waters were in equilibrium with the atmosphere when they sank, or at least the extent of disequilibrium is known.

Most current models reproduce the major features of ocean C, including vertical gradient of DIC, the seasonal patterns of pCO_2 in surface waters, the inter-annual variability in pCO_2 observed during El Nino (Gruber et al. 2009). On the other hand, ocean models fails to capture the spatial distribution of ^{14}C at intermediate and deeper depth (Orr et al. 2001), and interhemispheric transport of C suggested from atmospheric CO_2 measurements (Stephens et al. 1998). The models also have tight coupling between C and other nutrients which seems not have existed in past and may not exist in the future. A number of ocean C models have been used to determine annual uptake of anthropogenic C by global oceans (Gruber et al. 2009; Khatiwala et al. 2009; Le Quéré et al. 2010; Wanninkhof et al. 2013; Khatiwala et al. 2013).

Estimates of Air-Sea Fluxes of Anthropogenic Carbon Dioxide

The decadal ocean CO_2 sink has increased from 1.1 ± 0.5 Pg C yr^{-1} in the 1960s to 2.6 ± 0.5 Pg C yr^{-1} during 2004–2013 decade. The estimated average global anthropogenic CO_2 uptake from 1990 to 2009 is 2.0 ± 0.6 Pg yr^{-1} (Wanninkhof et al. 2013). In 2015 the estimated CO_2 flux from the atmosphere to the ocean (representing anthropogenic ocean C sink) was 3.0 ± 0.5 Pg C yr^{-1} (Table 6.3; Le Quéré et al. 2015, 2016), roughly in line with the atmospheric CO_2 concentration increase (Fig. 6.6), but with high inter-annual variations, showing an increased ocean sink during El Nino events (Roedenbeck et al. 2014). Changes in climate trends such as ocean warming, changes in circulation, changes in marine ecosystems and changes in biogeochemical cycles can also affect the oceanic CO_2 sink as well as the natural air-sea CO_2 fluxes. The uptake of anthropogenic CO_2 is limited mainly by the rate of transport from surface waters into deep ocean (Sarmiento and Sundquist 1992; Graven et al. 2012).

Analyses of regional observations indicates substantial spatial and temporal variations in air-sea CO_2 partial pressure, suggesting that the rate of ocean C storage does not seem to be keeping pace with the rate of growth in CO_2 emissions in all regions (Le Quéré et al. 2010; Wanninkhof et al. 2013). In the Northern Atlantic, observations suggest the ocean CO_2 partial pressure increasing at the faster rates than atmospheric CO_2 regionally, between 1990 and 2006 (Schuster et al. 2009), indicating decreasing sink for CO_2. The anomalous trend appears to be related to sea surface warming and its effects on CO_2 solubility and changes in ocean circulation. In the tropics the CO_2 partial pressure appears to have increased slower than the than the atmospheric CO_2 (Takahashi et al. 2006). Estimates indicate that about a quarter of the anthropogenic CO_2 emitted in the last 20 years was taken up by the ocean at a mean rate ranging from 2.0 to 2.5 Pg C yr^{-1} (Wanninkhof et al. 2013). Over hundreds to thousands of years, the oceans will be able to absorb as much as 70–80% of CO_2 released to the atmosphere, and ocean circulation becomes less limiting process and biology becomes important over these timescales (Archer et al. 1997). Thus, the role of oceans in controlling the atmospheric CO_2 concentration depends on the timescale being examined and the processes that dominate over these timescales.

The processes involved in in uptake of anthropogenic CO_2 by the oceans are subject to climate feedbacks. In the risk assessment of C cycling vulnerabilities, Gruber (Gruber et al. 2004) identified six climate associated feedbacks namely: (i) chemistry feedback—ocean pH falls as CO_2 is taken up, thereby altering the CO_2:DIC partition and reducing CO_2 uptake; (ii) ocean temperature—ocean temperature increase leads to similar positive feedback through CO_2:DIC partitioning; (iii) changes in deep ocean circulation—increasing vertical ocean water stratification increases ocean water equilibration time, inducing appositive feedback through reduced CO_2 uptake over timescales of 10–100 years since the mixing timescale becomes longer; (iv) ocean circulation changes—in addition to changing the equilibration timescale, changes in ocean circulation alter the equilibrium C distribution itself, and when coupled with the biological pump leads to a negative feedback due to reduced upward transport of DIC from deep waters to surface water while downward biological pump is not affected; (v) influence of climate change to the biological pump—the biological pump is subject to large influence by climate change. However, uncertainties are so high such that it is not possible to identify whether these influences add up to an overall positive or negative feedback; (vi) possibility of release from the large stores of CH_4 hydrates in sediments under continental shelves and permafrost. This constitutes a massive positive feedback on climate system through heating, but it is high risk—low probability scenario according to (Gruber et al. 2004). The surface dissolution and equilibrium CO_2 with the atmosphere varies with temperature [4.23% decrease per degree warming (Takahashi et al. 1993)] and increase in CO_2 concentration [about 15% per 100 ppm based on Revelle factor computation (Revelle and Suess 1957)].

Ocean Sink of Anthropogenic CO_2 During the Industrial Era

During the last few years, significant advances have been made in separating the anthropogenic component from the background of ocean dissolved CO_2. Ocean CO_2 Uptake of anthropogenic CO_2 in recent decades has been estimated at about a third of cumulative anthropogenic CO_2, with some indication that the oceanic C sink may have changed during the past few decades (Le Quéré et al. 2010), although significant uncertainties remain (McKinley et al. 2011). The weakening of the sink is attributed to enhanced upwelling, transport of C rich water, changes in wind patterns and ocean warming (Lovenduski et al. 2008; Le Quéré et al. 2010). The models estimate of the cumulative uptake of anthropogenic C by the world's ocean by 2010 at 155 Pg C (Khatiwala et al. 2013).

A global inventory of anthropogenic CO_2 uptake by the oceans from 1750 to 2015 is estimated at 175 ± 20 Pg C (Le Quéré et al. 2016), with the highest uptake in the mid-latitudes and lowest near the equator and high latitude of southern ocean (Sabine et al. 2004b). About 25% of the anthropogenic CO_2 is taken up by the North Atlantic, which is an important region of deep water formation, while another

~56% of the total anthropogenic CO_2 is stored in the southern hemisphere. The deep waters have not yet been exposed to the anthropogenic CO_2 mainly because of slow ventilation of deep waters.

These findings have main implications, suggesting that marine systems will continue to take up CO_2 as long as atmospheric CO_2 concentrations will continue to increase. However, since this reaction is not irreversible, the surface and near-surface waters will start to release part of the anthropogenic CO_2 to the atmosphere if the atmospheric CO_2 concentration was to decrease in the future. The implication to this process is the delayed decrease in the atmospheric CO_2 even if the anthropogenic CO_2 emissions were to decline or even stop in the future.

6.3.2.2 Land—Atmosphere Exchange Fluxes

The terrestrial C balance equates the net change in terrestrial-biosphere C to the sum of C fluxes into the terrestrial C pool, which include land-air gaseous exchange, waterborne and airborne particulate transport, and product removal by humans. However, this section focuses on land-atmosphere gaseous exchange which is the most significant for the global C cycle and C budget. Gaseous C exchange between terrestrial systems and the atmosphere occurs through fluxes of CO_2 and other C species such as CH_4, volatile organic C (VOCs) and CO. The CO_2 exchange dominates the mass flux, although other species have significant effects on radiative forcing (i.e., CH_4). Global change has focused on the emergence of the industrial processes in 1750 as the beginning of the critical period within which anthropogenic global change processes, including land use became significant forces driving changes in the Earth system globally (Kirch 2005; Johnsen et al. 1992). Prior to the Industrial revolution, gross photosynthetic C flux is estimated at 108.9 Pg C yr^{-1}, while total respiration and OM decomposition C flux from the terrestrial biosphere to the atmosphere is estimated at 107.2 Pg C yr^{-1} (Fig. 6.1; Beer et al. 2010). Elevated atmospheric CO_2 and increases in N deposition lead to higher leaf photosynthesis and reduced canopy transpiration causing increased plant water use efficiency (WUE) and reduced fluxes of surface latent heat. The increase in leaf photosynthesis with rising CO_2, also called CO_2 fertilization play a dominant role in global C sink (Sitch et al. 2008).

Human activities have altered, and continue to alter a broad range of C cycle processes. The land use, primarily deforestation, agriculture, land degradation and other form of land use change releases significant quantities of CO_2 and have also vastly changed the Earth's land cover by redirecting nearly a quarter of global net primary productivity (GNPP, i.e., the net rate of photosynthetic C uptake after plants have respired the CO_2 required for their own metabolism) to the production of food, fuel, fiber, and shelter (Haberl et al. 2007). Deforestation and soil degradation has enhanced the release of CO_2 from soils and dead plant biomass. Enhanced soil erosion rates and sediment deposition accelerate the exposure of soil OM.

The NPP or net photosynthetic activity by plants of a large land area is a unique integrator of climatic, ecological, geochemical, and human influences. There is substantial incentive to understand the magnitude and variability of the NPP, both for its role in C cycling and as the foundation of food, fiber, and fuel for human consumption and energy. Estimation of the NPP involves integration across the disciplines, bringing formidable challenges for long term monitoring. Unlike the direct measurement of properties such as atmospheric CO_2 or temperature, which are subject to small characterized instrumental and sampling errors, the NPP estimates are sensitive to a relatively broad range of errors and uncertainties that result from a variety of measurement techniques, spanning from methodological, physiological, ecological, and remote sensing techniques. Analysis us global vegetation response to climatic changes indicate a 6% increase in global NPP from 1982 to 1999 or 3.4 Pg C over 18 years globally, with the largest increase occurring in tropical ecosystems. Amazon forests accounted for 42% of the global increase in NPP, owing to decreased cloud cover which results in increase in solar radiation (Nemani et al. 2003). The anomaly in global NPP trend is closely related to the inverted anomaly of CO_2 growth rate. One of the most important properties defining the contribution of the terrestrial system to global C cycle is the net ecosystem CO_2 exchange [NEE, i.e., sum of total uptake of CO_2 by photosynthetic (plant respiration) and heterotrophic (decomposition of dead material) sources (Friend et al. 2007)].

It has been suggested that the excess of atmospheric CO_2 emission from fossil fuel burning and land use activities over that accounted for by accumulation in the atmosphere and ocean in the global C cycle, the so called "missing sink" in the global C cycle can be accounted for by enhanced accumulation of OC by terrestrial biosphere (Houghton et al. 1998). The terrestrial biosphere currently takes up about 25% of fossil fuel emissions of CO_2 or about 30% of the anthropogenic emissions, but unlike the ocean sink, the terrestrial CO_2 sink is highly variable from year to year (Friedlingstein et al. 2006; Le Quéré et al. 2015; Fig. 6.5), ranging from 0.3 to 5.0 Pg C (Canadell et al. 2007a). The uncertainties associated with both emissions from land use and sink are large. Given the international efforts to stabilize the atmospheric CO_2 concentrations and climate, the terrestrial sink can be viewed as a subsidy to global economies worth large sum of money. Because many aspects of the terrestrial sink are amenable to purposeful management, its basic and dynamics needs to be well understood.

Land plants have been storing greater amount of C through CO_2 fertilization effect on photosynthesis as a result of increasing atmospheric CO_2 concentration, warmer temperatures, and increased N deposition and P inputs to the terrestrial ecosystem (Houghton et al. 1998; Bonan and Levis 2010; Zaehle and Dalmonech 2011). The oceans are known to have important role of regulating the climate on annual to millennial scales by absorbing CO_2 and exchanging C with various C storing reservoirs, such as the atmosphere, the land, the biota, and fossil fuel C pool. The process affecting the net land-atmosphere flux of CO_2 can be grouped into three classes: (i) changes in atmospheric composition, (ii) changes in physical climate, and (iii) changes in land use and land management (Table 6.5).

Changes in atmospheric composition include CO_2 fertilization effects, fertilization by N deposition, and effects of pollution (Table 6.5). Physiologically, plants respond to rising atmospheric CO_2 with increased assimilation, leading to increased

Table 6.5 Processes contributing to net land-atmosphere exchange of CO_2

Process	Source (+) or sink (−)
Changes in atmospheric composition	
• CO_2 fertilization	Sink (−)
• Nutrients constraints on CO_2 fertilization	Source (+)
• Fertilization by N deposition	Sink (−)
• Pollution effects (e.g., acid rain, ozone, etc.)	+ or −
Changes in physical climate	
• Warming and moisture response of the respiration	+
• Net primary productivity (NPP) response to warming and moisture	−
• Effects of radiation (e.g., direct vs. diffuse)	−
• Biome shifts	+ or −
• Permafrost thawing	+
• Wild fires regime change	+
• Changes in herbivore ecology (e.g., insects and pests)	+
Changes in land use and land management	
• Deforestation and land clearing	+
• Managed afforestation and reforestation	−
• Unmanaged forest regrowth after cropland abandonment	−
• Managed fire regime change	+
• Woody encroachment and woody thickening	−
• Peatland and wetland drainage	+
• Agricultural practices	+ or −

Source Canadell et al. (2007a)

biomass. However, field results from free air CO_2 enrichment (FACE) and other elevated CO_2 studies have shown variable results with some species sustaining higher rates of C accumulations over multiple years and diminishing or lack of CO_2 fertilization effect in some species and ecosystems (Oren et al. 2001; Norby et al. 2005, 2010; Zak et al. 2011; Newingham et al. 2013). Field observations also indicate saturation of response to CO_2 fertilization at 500–600 ppm, much lower than expected on physiological grounds. The CO_2 fertilization may not be manifested in most field environments because of possible constraints from other factors other than CO_2, especially N limitation and interaction between water limitation and CO_2 fertilization. Significant enhancement of the terrestrial CO_2 sinks by N deposition has been suggested, especially in mid-latitude Northern Hemisphere forests where N limitation is common and N deposition rates are high (Holland et al. 1997). An estimated terrestrial sinks of 0.25 Pg C yr^{-1} has been suggested as a result of N deposition (Nadelhoffer et al. 1999). However, it is unlikely that N deposition will create major new sink over the next century (Canadell et al. 2007a).

The changes in climate have significant influence on heterotrophic respiration, soil moisture and NPP, among other factors (Table 6.5). Warming increases respiration of soil C, most notably the fast turnover C pools (Fang et al. 2005).

Warming also increases terrestrial NPP, due to extension of the growing season. An estimated global terrestrial NPP increase of 6% or 3.5 Pg C yr^{-1} over two decades from 1981 to 2000 has been attributed to extension of the growing season in high-northern latitude ecosystems (Nemani et al. 2003). However, decrease C uptake as a result of hotter and drier summers seems to cancel the C uptake gain resulting from extension of growing season (Angert et al. 2005). Permafrost, another factor associated with warming could shrink by as much as 25% and release both CO_2 and CH_4 with mean global warming of 2 °C (Anisimov et al. 1999).

6.3.2.3 Land—Ocean Carbon Fluxes

Rivers are the major conduits of water, nutrients, minerals, and C from land to the oceans. Soil water, groundwater, and runoff slowly find their way into rivers, and dissolved C contained in these water is transported by rivers to the oceans in the form of DIC, dissolved organic C (DOC), and particulate C. Some C is also released as CO_2 in river channels and estuaries. Therefore, the amount of C that enters the oceans is smaller than the estimates from the river flow. Land use change and land management activities including soil erosion, liming, fertilizer, herbicides and pesticides application, sewage water production, damming of water courses, water withdrawal, and human induced climatic change have modified the delivery of elements through the aquatic continuum that connects soil water to open ocean through rivers, streams, lakes, reservoirs, estuaries, and coastal zones with major impact on global biogeochemical cycles (Aumont et al. 2001; da Cunha et al. 2007; Quinton et al. 2010). The C is transferred through the aquatic continuum laterally across ecosystems and regional geographic boundaries as well as exchange vertically between the transport channel and atmosphere, often as CO_2. The importance of the aquatic continuum from land to the ocean in terms of its impact on lateral C fluxes has been known for more than two decades (Sarmiento and Sundquist 1992). However, the magnitude of its anthropogenic perturbation has only recently became apparent (Cole et al. 2007; Battin et al. 2009; McLeod et al. 2011). The lateral transport of C from land to sea has long been regarded as a natural loop in the global C cycle unaffected by anthropogenic perturbation, and thus neglected in assessment of the CO_2 budget (Peters et al. 2012; Le Quéré et al. 2009) as well as for closing the C budget of the ongoing anthropogenic perturbation. The major challenges in the study of C in aquatic continuum include the differentiation of the anthropogenic perturbation from the natural transfers, identifying the drivers responsible for the ongoing changes, and ultimately incorporating these processes in Earth system models and establish policy-relevant budget and mitigation strategies (Regnier et al. 2013). Riverine supply C of largely terrestrial origin is important to the steady-state chemistry of the ocean. The riverine C fluxes from land to ocean are generally well correlated with river discharge, except in regions where factors such as high peat and CO_3^{2-} and high erosion rates in watersheds also control C inputs (Raymond et al. 2007; Dai et al. 2012).

Based on upscaling of local C budgets, the present-day bulk C input to freshwaters (natural plus anthropogenic) was estimated at 2.7–2.9 Pg C yr^{-1} (Battin et al. 2009; Tranvik et al. 2009). This input consists of four fluxes (i) soil-derived C that is released to inland waters, mainly as organic form, both particulate and dissolved, and also as free dissolved CO_2 from soil respiration estimated at 1.9 Pg C yr^{-1}, (ii) chemical weathering of continental surfaces—carbonate and silicate, which is part of geological inorganic C input to upstream rivers which is estimated at 0.5 Pg C yr^{-1} (Hartmann et al. 2009), (iii) C dissolved in sewage water originating from biomass consumption by humans and domestic animals estimated to release additional 0.1 Pg C yr^{-1} as an input to freshwaters (Prairie and Duarte 2007), (iv) photosynthetic C fixation within the inland waters—substantial part of this is returned to the atmosphere through decomposition within inland waters, but a small proportion remains for export to oceans and burial (Downing et al. 2008). About 0.2—0.6 Pg C yr^{-1} is buried in aquatic sediments, 0.8–1.2 Pg C yr^{-1} returns to the atmosphere as CO_2, and 1.0 Pg C yr^{-1} is delivered to the ocean (Battin et al. 2009; Aufdenkampe et al. 2011).

Model simulations suggest that the riverine transport of C has increased by about 20% from 0.75 Pg C yr^{-1} in 1750 to 0.9–0.95 Pg C yr^{-1} at present (Regnier et al. 2013). The increase is attributed to deforestation and more intensive cultivation practices that have increased soil degradation and soil erosion. The accurate quantification of anthropogenic perturbation of land to ocean flux remains challenging, but it is estimated that during the industrial era, the land use changes are the main driver of the anthropogenic alteration of land to ocean C flux perturbation. The extra anthropogenic C delivered to the continuum of land-ocean aquatic system is estimated at 1.1 Pg C yr^{-1}, of which, 0.8 Pg C yr^{-1} is from soils, 0.1 Pg C yr^{-1} is from weathering, 0.1 Pg C yr^{-1} is from sewage, and 0.1 Pg C yr^{-1} from enhanced C fixation in inland waters (Regnier et al. 2013).

Rivers and groundwater from terrestrial continents are important transporters of C from continents to the oceans. Rivers also move inorganic C products such as carbonates formed from rock weathering to oceans. However the estimates of C transfers to the oceans are complicated by the dynamics of C compounds and the scarcity of data. Groundwater discharge to oceans makes up as high as 10% of the surface flow to the oceans, but its contribution to C import to oceans is poorly known. Humans have increased significantly C and other nutrients (particularly reactive N and P) concentrations in rivers. Through intensified land use, up to 100 times more sediment and associated C is transported to oceans compared to pre-cultivation (Sabine et al. 2004c). Not all of OC moves passively through rivers, however. Part of OC is mineralized during the transport, and it leads to elevated CO_2 concentrations in the rivers, lakes, and estuaries. Some portion of OC may be transported as recalcitrant C or retained in the sediments as particulate OC. Estimated anthropogenic C exported to oceans through soil erosion is $\sim$1.5 Pg C yr^{-1} and about 1.0 Pg C yr^{-1} is lost as CO_2 via river outgassing. The annual global net transport rate of C to oceans are $\sim$0.4 Pg C yr^{-1} as dissolved inorganic C, 0.2 Pg C yr^{-1} particulate inorganic C, 0.3 Pg C yr^{-1} dissolved OC, and 0.2 Pg C yr^{-1} particulate OC (Chen 2004).

The changing global C cycle is viewed as the primary driver of climate change and also as a primary source of the uncertainty in projecting future climate trends. For example, thawing of permafrost, warming of northern peat lands and boreal forests, which is a significant storage of terrestrial C result in dramatic changes in terrestrial ecosystems (Schuur et al. 2008; Ise et al. 2008). Significant quantities of C in these and other environments may also be vulnerable to fires and accelerated decomposition under warmer conditions, potentially releasing large quantities of CO_2 to the atmosphere.

6.4 The Global Carbon Budget

On century and multi-decadal time frame, increasing global atmospheric CO_2 is attributed to $FFCO_2$ and LULCC emissions (Fig. 6.5; Boden et al. 2016; Le Quéré et al. 2015, 2016). Average decadal $FFCO_2$ emissions for 1980–1989, 1990–1999, and 2000–2009 were 5.5 ± 0.3, 6.3 ± 0.3, and 8.0 ± 0.4 Pg C yr^{-1}, respectively (Table 6.3). Although the $FFCO_2$ emission has been increasing, it has been suggested that cumulative emissions for the period 1994–2007 has been underestimated by as much as ~9 Pg C (Francey et al. 2013). Global $FFCO_2$ emissions for 2010, 2011, 2012, 2013 and 2014 were 9.17 ± 0.8, 9.46 ± 0.8, 9.67 ± 0.8, 9.89 ± 0.8 and 10.1 ± 0.8 Pg C yr^{-1}, respectively, and global financial crisis induced only a short-lived decline in CO_2 emissions in 2008–2009 which return to high annual growth rate in 2010 (Fig. 6.5, Peters et al. 2013; Boden et al. 2016). From 1750 to 2015, the $FFCO_2$ emissions is estimated at 410 ± 20 Pg C (Table 6.6, Boden et al. 2016; Le Quéré et al. 2015, 2016).

The LULCC CO_2 emissions is partly offset by other land uses such as afforestation, vegetation regrowth on abandoned lands, and other deliberate land management activities that enhances SOC storage on land such as cover crops in agricultural lands. The net flux from the terrestrial sources is the balance among

Table 6.6 The global C budget for the period 1750–2015

Sources	1750–2015 (Pg C)	Reference
Fossil fuel combustion and cement production	410 ± 20	Boden et al. (2016), Le Quéré et al. (2016)
Land-use change emissions	190 ± 65	Giglio et al. (2013), Houghton et al. (2012)
Total emissions	600 ± 70	
Atmospheric increase	260 ± 5	Dlugokencky and Tans (2016)
Ocean uptake	175 ± 20	Le Quéré et al. (2015, 2016)
Residual terrestrial sink	165 ± 70	Le Quéré et al. (2015, 2016)
Net terrestrial source	25 ± 70	

terrestrial sources and sink processes. Currently the net land use is globally a net source to the atmosphere (Table 6.6). Over the period of 1750–2013, the cumulative emissions from LULCC is estimated at 190 ± 65 Pg C (Ciais et al. 2013; Houghton et al. 2012; Le Quéré et al. 2015, 2016).

Of the total emissions (FFCO$_2$ + LULCC CO$_2$) estimated at 600 ± 70 Pg C for the period of 1750–2015, 260 ± 5 Pg C was retained in the atmosphere (Table 6.6), and atmospheric CO$_2$ concentration increased at annual rate ranging from 0.5 to 2.8 ppm yr^{-1} from 1959 to 2015 (Fig. 6.7, Dlugokencky and Tans 2016). The remaining CO$_2$ was absorbed by the oceans and terrestrial sink. The ocean sink is estimated to sequester ~30% of the anthropogenic CO$_2$ emissions (Tables 6.3, 6.6), albeit with environmental costs associated with this service, such as ocean waters acidification (Ballantyne et al. 2015). The inverse calculations show that tropic region is currently a moderate source, largely oceanic C as a result of outgassing in upwelling regions, with some terrestrial sources also. The estimates vary greatly however, depending on the models of atmospheric transport, and years included in analyses. For the period 1992–1996, the global oceanic sink of 1.3 Pg C yr^{-1} distributed in Northern (1.2 Pg C yr^{-1}) and Southern (0.8 Pg yr^{-1}) with a net source from tropical gyres (0.5 Pg C yr^{-1}) was reported (Gurney et al. 2002). The terrestrial sink for this period was estimated at 2.4 ± 0.8 and 0.2 Pg C yr^{-1} for the northern and southern mid-latitude lands, respectively, with some offset by a net tropical land source of 1.2 ± 1.2 Pg C yr^{-1} (Gurney et al. 2002). Errors are larger for tropics because of lack of sampling stations and more

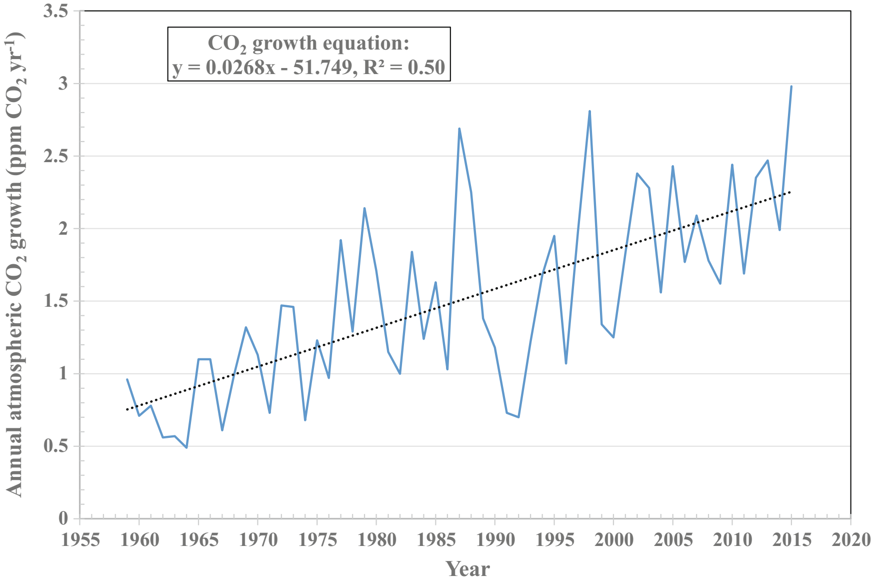

Fig. 6.7 Annual atmospheric CO$_2$ increase from 1959 to 2015. *Data source* Dlugokencky and Tans (2016)

complex atmospheric circulation. A more recent synthesis estimates that temperate zone and boreal forests of both northern and southern hemisphere were a net sink of 0.91 Pg C yr^{-1} during 1990s and 1.03 Pg C yr^{-1} between 2000 and 2007, about 40% of the global sink (Pan et al. 2011). The C inventories of non-forest lands are generally lacking, although there are suggestions at least from US that non-forest may account for 40–70% of the terrestrial sink (Houghton 1999; Pacala et al. 2001). Accumulation of C below ground may also be greater than assumed or modeled in analyses based on forest inventories. Few studies that have measured C in forest soils have suggested that forest soils accounts for small 5–15% of measured ecosystem C sinks (Schlesinger and Lichter 2001; Kurz et al. 2013). Overall, the terrestrial ecosystems are currently a net sink of atmospheric CO_2, and this global sink has intensified from neutral CO_2 flux of 0.1 ± 0.8 Pg C yr^{-1} in 1980s to a net sink of 1.1 ± 0.9 and 1.5 ± 0.9 Pg C yr^{-1} in 1990s and 2000s, respectively (Table 6.3, Gurney and Eckels 2011).

6.5 Conclusions

Within a few centuries, anthropogenic activities are returning to the atmosphere and oceans a large quantities of concentrated organic carbon stored in sedimentary rocks over hundreds of millions of years. The last two and half centuries have seen 43% increases in the amount of C in the atmosphere, with most of it occurring in the last 150 years. Although most of this C has come from the combustion of fossil fuels, an estimated 120–250 Pg C has been lost from the terrestrial ecosystems as a result of human management between 1750 and 2013. The global C balance suggests that the terrestrial ecosystem has accumulated 20–30 Pg C since about 1930s at a steadily increasing rate. This terrestrial sink is not permanent feature of terrestrial biosphere but the result of imbalance driven by past and present human activities. The sink strength shows high inter-annual variability, and the evidence shows that the sink cannot be sustained indefinitely. Plausible processes that can explain the current terrestrial sink are land use change, including forest regrowth on abandoned croplands, fire exclusion, and responses of ecosystem C storage to related increases in atmospheric CO_2, N deposition, and climate change among other processes acting individually, synergistically and some antagonistically. Some sink processes will saturate at higher atmospheric CO_2 levels expected to be reached in the next few decades to centuries. Therefore overall, the terrestrial sink in inherently temporary, which will disappear over time. High C density regions on land—such as permafrost and peatlands are also vulnerable to global warming and likely to add C in the atmosphere in the coming decades. The annual net fluxes of C are small relative to the sizes of the reservoirs but the fluxes have been accelerating. The major drivers of C cycling are reasonably well known. Future research should address:

- Integrated key sink processes for regional and global C budgets and provide the important regional processes to guide mitigation policies.
- Integration of past land use changes—such as forest age structure in biogeochemical models.
- Extent of new sinks created by afforestation, reforestation and land aggrading.
- Sensitivity of SOM pools (i.e., heterotrophic respiration) to temperature and moisture effects.
- Accurate assessment of vulnerable C pools to climate changes and land use changes.
- Increasing the sophistication and sensitivity of C cycling models in coupled carbon-climate with the inclusion of land surface processes such as vegetation shifts, anthropogenic and wild fires, nutrients feedback, and vulnerable C pools.

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Chapter 7
Historical and Contemporary Global Methane Cycling

Abstract Methane (CH_4) has been studied as an atmospheric constituent for more than 200 years. However, the first modern measurements of atmospheric CH_4 concentration were made by using the infrared absorption and estimated an atmospheric concentration of 2.0 ppmv in 1948. The development of gas chromatography (GC) and the flame ionization detector (FID) in the 1950s led to observations of vertical CH_4 distributions in the troposphere and stratosphere, and to establishment of time-series sampling programs starting from 1979. Results from these sampling programs led to suggestions that similar to atmospheric CO_2, the concentration of atmospheric CH_4 has been increasing. The data indicated that the atmospheric CH_4 concentration has increased almost exponentially from 722 ± 4 ppb at the onset of Industrial Revolution in 1750 to 1650 ppb by mid 1980s when global CH_4 emissions monitoring started. The current (2015) global annual surface mean abundance is 1845 ± 2 ppb, and a relative abundance of 256% compared to 1750. The mean annual absolute increase during the last 10 years is estimated at 6 ppb CH_4 yr^{-1}. The role of CH_4 as one of the greenhouse gas (GHG) causing global warming stimulated further research on sources and sinks of CH_4, which is emitted from a variety of sources, both of natural and anthropogenic origin. Natural sources account for about 40% of the total, while anthropogenic emissions contributing 60% of the global emissions. The anthropogenic sources fall under the main categories of agriculture, energy, waste, and industry. CH_4 is also of interest to microbiologists, but findings from microbiology have entered the larger context of the global CH_4 budget only recently. CH_4 is the most abundant hydrocarbon in the atmosphere, and its increase by a factor of 2.5 since the Industrial Era has raised concerns due to the potential effects on atmospheric chemistry and climate. It plays important roles in atmospheric chemistry and the radiative balance of the Earth. Stratospheric oxidation of CH_4 provides a means of introducing water vapor above the tropopause. The CH_4 also reacts with atomic chlorine in the stratosphere, forming HCl, a reservoir species for chlorine. Some 90% of the CH_4 entering the atmosphere is oxidized through reactions initiated by the OH radical, mostly in the troposphere. These reactions are important in controlling the oxidation state of the atmosphere. The CH_4 absorbs infrared (IR) radiation in the troposphere and is an important GHG. On per mole basis, CH_4 is more effective a GHG than CO_2. Current atmospheric burden is estimated at 4954 ± 10 Tg CH_4,

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with the annual increase estimated at 14 ± 3 Tg CH_4 yr^{-1} from both natural (36.3%) and anthropogenic (63.7%) sources.

Keywords Terrestrial methane studies · Marine methane studies · Ice cores · Methanotrophic organisms · Methanogenesis · Dansgaard-Oeschger event

Contents

7.1 Introduction

Oxidation of CH_4 has been a subject of scientific inquiry since 1776, when Alexandro Volta (1745–1827), an Italian physicist described the first experiments of flammable air released by shallow sediments in Lake Maggiore in a letter to Father Carlo Campi (Wolfe 2004). Subsequently, CH_4 was exploited as a source of heat and light (King 1992). Despite its commercial significance, the biological and ecological aspects of CH_4 oxidation did not gain attention until the pioneering work of Söhngen, who isolated CH_4-oxidizing bacteria in 1906. Little additional progress was made until 1960s when systematic efforts of several groups provided the methodological tools and detail taxonomy, physiology and biochemistry of methanogenic metabolism (King 1992). Among other motivations, this work was stimulated by the potential role of methanotrophic bacteria in food spoilage and by possible use of methanotrophs in bioremediation of certain halogenated organic pollutants or agents of commercial biotransformation (Higgins et al. 1980). The critical role of CH_4 in atmospheric chemistry and Earth's energy budget has stimulated environmental and ecological research since early 1990s (Crutzen 1995).

CH_4 is the most abundant hydrocarbon in the Earth's atmosphere, which plays important roles in atmospheric chemistry and radiative balance of the Earth. Next to H_2O and CO_2, CH_4 is the most abundant long-lived greenhouse gas (GHG) which absorbs infrared radiation in the troposphere (Ramanathan et al. 1985). Both on molecule and mass basis, CH_4 is much more effective GHG than CO_2. These gases absorb long-wave radiation emitted by Earth's surface in the 4–100 μm atmospheric window and hence affect atmospheric temperature directly by shielding heat loss and causing global warming (Hansen et al. 1988; Ramanathan 1988). Emission of CH_4 has caused radiative forcing of 0.97 W m^{-2} since 1750, about twice as much as the direct CH_4 concentration based estimate of 0.48 ± 0.05 W m^{-2} (Hofmann et al. 2006; Stocker et al. 2013). The difference in estimate is caused by the indirect impacts on CO_2, stratospheric water vapor, ozone (O_3), sulfate aerosol, and the change in lifetimes of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) (Boucher et al. 2009). The anthropogenic CH_4 is contributing 17–20% to the total radiative forcing induced by the long-lived anthropogenic GHGs from 1750 to 2013 (Myhre et al. 2013; Kirschke et al. 2013). A recent estimate of atmospheric lifetime of CH_4 ranges from 9.8 ± 1.6 to 11.2 ± 1.3 years (Dlugokencky et al. 2009; Myhre et al. 2013), and its emission reduction would have immediate benefit to global climate. The global warming potential (GWP) of CH_4 is 28 (i.e., it is 28 times more efficient per mass as GHG) compared to CO_2 over a 100-year period (Myhre et al. 2013).

It is most the abundant chemically reactive trace gas in the troposphere important to chemical state of atmosphere due to its chemical destruction by reaction with the hydroxyl radical (OH) that influences the abundance of ozone (O_3) in the troposphere and stratosphere (Johnston 1984) and affect tropospheric air quality. It is also a major source of stratospheric water (Pollock et al. 1980). In the troposphere, CH_4 is oxidized to CO and ultimately to CO_2 and H_2O in oxidation sequence initiated by hydroxyl (OH) radical. These reactions constitute the main sink for atmospheric CH_4 (Ehhalt and Heidt 1973). By reacting with OH radicals, CH_4 reduces the oxidizing capacity of the atmosphere and generates O_3 in the troposphere. Stratospheric oxidation of CH_4 provides the means of introducing water vapor above the tropopause (Wofsy 1976), and therefore, long term increase in atmospheric CH_4 leads to an increased anthropogenic forcing from water vapor in the stratosphere. Stratospheric water vapor increased by 1.0 ± 0.2 ppm during 1980–2010, and CH_4 oxidation explains approximately 25% of this increase (Hurst et al. 2011). About 90% of the CH_4 entering the atmosphere is oxidized through reactions initiated by OH radical.

Formation of tropospheric OH is initiated by photo-dissociation of O_3, followed by reaction with water vapor which creates sensitivity to humidity, cloud cover, and solar radiation (Crutzen 1973). The other source of OH is through secondary reactions, especially oxidation of volatile organic compounds, notably isoprene in low-NO_x air (Lelieveld et al. 2008). Some of these reactions and chemistry underpinning them are still poorly understood (Taraborrelli et al. 2012). However,

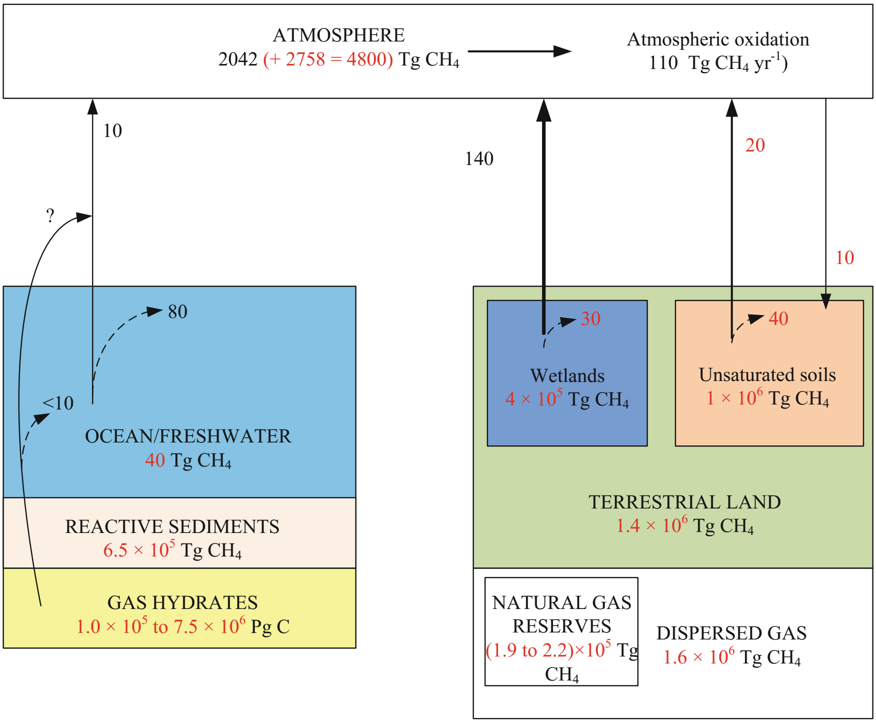

Fig. 7.1 Methane sub-cycle of the carbon cycle showing estimated methane reservoirs (Tg or Pg CH_4) and fluxes (Tg CH_4 yr^{-1}) of the pre-industrial period. *Data source* Sundquist and Ackerman (2014), Paul and Dillon (2001)

these reactions are important in controlling the oxidation state of the atmosphere. The chemical coupling between OH and CH_4 leads to significant amplification of CH_4 emission impacts such as increased CH_4 atmospheric lifetime and the atmospheric CH_4 burden. The CH_4 is also the primary sink for chlorine radicals (Cicerone and Oremland 1988).

In addition to changes in atmospheric chemistry and radiative balance of the Earth's atmosphere, CH_4 plays a role in the global C cycle (Fig. 7.1), and is also an important component of natural biogeochemical cycles. CH_4 is also an important source of environmentally cleaner energy for modern society. Numerous direct roles of CH_4 to further impact climate, atmospheric chemistry, and biogeochemistry of land and ocean and also the energy needs have made the study of CH_4 biogeochemistry an urgency, far beyond the scientific curiosity. Therefore, understanding changes in its atmospheric concentration is an indication of understanding the underlying biogeochemistry and its reaction to external changes. A portion of organic matter (OM) that enter diverse O_2-free (e.g., anaerobic) environments such as wetlands, subsurface environments including hydrocarbon deposits and deep granitic aquifers and rumen of animals is recycled by methanogenic microorganisms to CH_4, which can be emitted to atmosphere or diffuses to aerobic zone and oxidized by methanotrophic organisms to CO_2.

The first quantitative measurements of atmospheric CH_4, both involving combustion and gravimetric determination of trapped oxidation products were reported in France by Boussingault (1834, 1864). Gautier (1901) estimated CH_4 concentrations of 10 and 0.28 ppmv on seashore and 95 ppmv in Paris. The first modern measurements of atmospheric CH_4 were the infrared absorption measurements which estimated an atmospheric concentration of 2.0 ppmv (Migeotte 1948). Development of gas chromatography (GC) and the flame ionization detector (FID) in 1950s led to observations of vertical CH_4 distributions in the troposphere and stratosphere, which led to an establishment of time series sampling programs. The first observation of a possible atmospheric CH_4 increase were reported by (Graedel and McRae 1980) when they analyzed 10-years continuous record of total hydrocarbon data collected at the New Jersey Department of Environmental Protection. However, an increasing trend in daily and annual minima was advanced somewhat tentatively due to concerns about the calibration technique, urban locations, and the fraction of total hydrocarbon attributable to CH_4. Rasmussen and Khalil (1981) used 22 months of an automated GC/FID measurements of atmospheric CH_4 at Cape Meares, Oregon to show a concentration increase of 2% yr^{-1} and similar trend for northern hemisphere data from 1965 to 1980. Cape Meares station has operated since 1979, and the techniques used by Rasmussen and Khalil (1981) were used to establish the National Oceanic and Atmospheric Administration (NOAA) network of global sampling for analyzing atmospheric CH_4 concentrations.

The current CH_4 emissions are of both natural and anthropogenic sources. Natural sources account for about 40% of the global emissions, whereas 60% comes from anthropogenic sources (Ciais et al. 2013). Anthropogenic sources are the result of agriculture, energy, waste, and industrial production, which contribute 50.63, 28.65, 20.61 and 0.10% of the anthropogenic sources, respectively (Karakurt et al. 2012). The increase in number of ruminants and expansion of rice paddy agriculture are the dominant agricultural sources, while coal mining and leakage from natural gas wells and supply system are attributed to fossil fuels. The emissions from landfills and waste are the dominant urban sources. Total anthropogenic emissions contribute between 50 and 65% of the total CH_4 sources. Enteric fermentation (agriculture), landfills and energy are the dominant sources in the United States (EPA 2015).

CH_4 is produced by bacteria under anaerobic conditions in wet environments such as wetlands, swamps, bogs, ferns, tundra, rice paddies, and landfills. CH_4 emitted from inundated anoxic environments can substantially be reduced by bacterial oxidation of CH_4 in oxic layers above. A small sink can be attributed to bacterial oxidation on relatively dry soils (Born et al. 1990) which relies on consumption of atmospheric CH_4. It is also produced in the stomachs of ruminants (i.e., cattle and other cud chewing mammals) and termites. Most of this biogenic CH_4 is generated by two major bacterial pathways: (i) fermentation of acetate, and (ii) reduction of CO_2 with H_2 (Whiticar et al. 1986; Cicerone and Oremland 1988).

Some of the emitted CH_4 is exported to the stratosphere. The same oxidation reactions which occurs in the troposphere also occurs in the lower stratosphere, and is initiated by OH. At higher altitudes, reactions with exited O_2 atoms (O^1D) and with chlorine atoms lead to mixing ratio profiles that decrease with increase in altitude. The atmospheric increase in CH_4 during the industrial Era is mostly attributed to anthropogenic activities. Higher concentrations of CH_4 have been observed above and downwind of densely populated and intensive agriculture areas where anthropogenic emissions occur (Frankenberg et al. 2011).

Although CO_2 emission and its mitigation dominate much of climate change research and policies, there is an increasing recognition that CH_4 emissions may often provide cost effective and more efficient means to mitigate anthropogenic climate change. In addition, current projection of GHG concentrations and resultant climate forcing in the 21st century require an improved understanding of how natural CH_4 sources will respond to changes in climate. Therefore, this chapter provides a synthesis of scientific understanding of major global sources of CH_4 and projections of how these emissions may change in response to the projected climate change.

The objectives of this chapter are to examine the past trends in the CH_4 concentrations, determine the sources and sinks affecting its atmospheric growth rate, and elucidate factors that could affect its future atmospheric growth rate. The chapter also examines the current underlying chemistry and its role as sub-cycle of the global carbon cycle.

7.2 Atmospheric Methane

Systematic measurements of CH_4 in the atmosphere began rather recently compared to those of atmospheric CO_2 (i.e., 1978, Dlugokencky et al. 1994). Therefore, to establish the extent of recent increases in its atmospheric concentration, the natural variability, and the processes underlying natural changes, it is necessary to identify other ways to establish its evolution with time. Polar ice acts as a natural gas archive, which preserves samples of ancient atmospheric air from which the concentration of stable trace gases can be measured directly (Raynaud et al. 1993; Stauffer et al. 2002). On the polar plateaus of Antarctica and Greenland, snow generally does not melt, but is compressed by weight of overlying new snowfall, and eventually turning to solid ice with enclosed air bubbles that becomes isolated from the overlying atmosphere at a depth ranging from 60 to 100 m depending on the snow accumulation rate and temperature (Wolff 2011). Because the snow remains permeable to air for several years until the close-off, the air trapped in ice cores is older than the air above the snow surface but much younger than the ice that enclose it due to air diffusion to snow pack prior to close-off which causes smoothing (Joos and Spahni 2008; Köhler et al. 2011). As a result, a given depth contains bubbles with an age distribution. The age distribution within a given ice core layer (e.g., Holocene at Dome C in Antarctica) will be typically 400 years (Schwander and Stauffer 1984), and this is what controls the resolution that can be achieved from ice core CH_4 concentration analysis (Wolff 2011).

7.2.1 Variability of Methane Concentration During Glacial-Interglacial Cycles

The history of atmospheric CH_4 mixing ratios has been reconstructed from measurements of air bubbles trapped in ice cores, and ice core records of trace gases are currently available over the period extending as far back as 800,000 years, and covering eight glacial-interglacial cycles (Augustin et al. 2004; Loulergue et al. 2008b). The concentration of CH_4 determined from ice cores during this period stayed within natural limits, with glacial concentration ranging from 320 to 400 ppb which then increased to maximum values ranging from 600 to 800 ppb during interglacial periods (Fig. 7.2a; Loulergue et al. 2008b; Wolff 2011). During glacial and interglacial times, large natural variations are also observed over different timescales. Figure 7.2b shows the variability of the ratio of deuterium to H (i.e., δD) of CH_4 from ice cores during the glacial/interglacial period. Similar to CH_4 cycles, the climate record of the past 800,000 years is dominated by the alteration between relatively short warmer interglacial periods and much longer cold glacial periods for both Greenland and Antarctica as revealed by temperature reconstructed from deuterium profile (Fig. 7.2c; Jouzel et al. 2007). Both CH_4 and reconstructed temperature cycles recur at about 100,000 years intervals (Loulergue et al. 2008b). The CH_4 concentration also shows sharp millennial changes of the order of 200 ppbv (Flückiger et al. 2004; Loulergue et al. 2008a).

The most conspicuous feature of the Vostok data is the close similarity among trends in CH_4 and local temperature reconstructed from the ratio of deuterium to H_2 in the ice (Fig. 7.2a, c). The most recent four cycles show long glacial period with short interglacial periods, and a temperature difference range for Antarctica of around 10 °C between warm and cold temperatures (Fig. 7.2c; Petit et al. 1999; Augustin et al. 2004). The patterns of Antarctic climate seen in the ice cores is also seen in other climate records around the world, (e.g., Lisiecki and Raymo 2005). The data revealed that maximum and minimum temperatures and CH_4 concentrations were nearly similar during each of eight glacial cycles, including the Holocene Epoch prior to human influence, which demonstrates the fact that similar to CO_2, CH_4 has contributed significantly to glacial/interglacial climate change. The abrupt climate change on timescales of 10–100 years resulting into CH_4 variability of 50–200 ppbv, and sharp climate jumps, which in Greenland can have an amplitude as high as 15 °C (Huber et al. 2006), termed as Dansgaard/Oeschger climatic events coinciding with summer insolation in the Northern Hemisphere, are also widespread throughout glacial/interglacial cycles (Severinghaus et al. 1998; Flückiger et al. 2004). The drivers of these changes are not well understood, but some indications suggest that they involve changes in ocean heat transport (Stocker and Johnsen 2003).

The isotopic ratio measurements from the ice cores ($^{13}CH_4$) provide constraints on mechanisms responsible for temporal changes in CH_4 concentration. The $\delta^{13}CH_4$ is also useful for separating different sources of CH_4, since different CH_4 sources have characteristic $\delta^{13}C$ signatures (Quay et al. 1999). The $\delta^{13}CH_4$ and

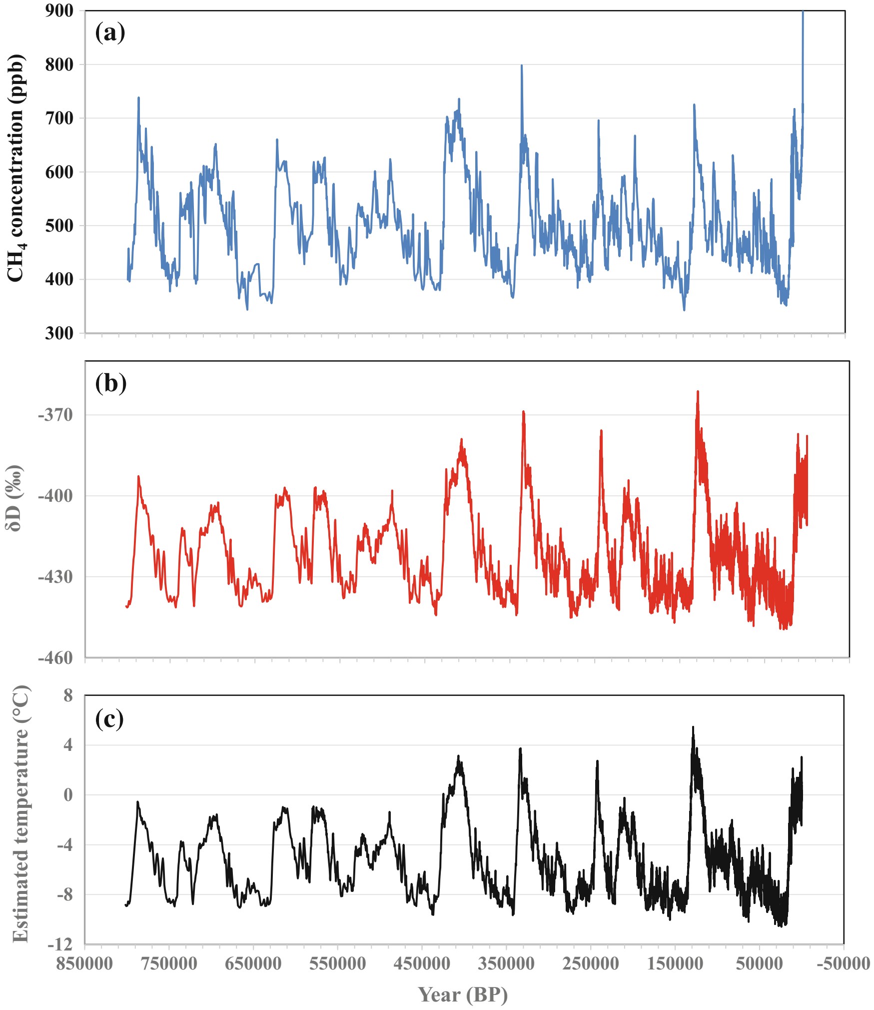

Fig. 7.2 The CH_4 (**a**), deuterium (**b**), and estimated temperature (**c**) fluctuations during glacial/interglacial cycles. *Source* Flückiger et al. (2004), Loulergue et al. (2008a, b), Parrenin et al. (2013)

deuterium (δD) ratio of CH_4 suggest that most of atmospheric CH_4 concentration increase during the interglacial period was the result of increased emissions from boreal and tropical wetlands and/or changing CH_4 sinks, most notably increased atmospheric CH_4 residence time due to reduced oxidative capacity of the atmosphere (Fischer et al. 2008). However, possible influence of other sources (i.e., marine CH_4 hydrates, biomass burning, and vegetation) must also be considered. Modeling studies suggest that temperature influence on tropical wetlands and global vegetation were the dominant controls of changes in atmospheric CH_4 concentration during glacial/interglacial period (Konijnendijk et al. 2011).

7.2.2 *Methane Concentrations During Holocene*

During the Holocene period, the interglacial which began ~11,700 years ago, the atmospheric CH_4 concentration decreased from near 700 ppb during the early periods of Holocene ~10,000 years, reaching the lowest concentrations of 570 ppb at about 5500 years, followed by an increase to 700 ppb in the pre-industrial time (Fig. 7.3a; Blunier et al. 1995; Flückiger et al. 2002). These changes are gradual, and not similar to Dansgaard-Oeschger event in Greenland climate and CH_4 or glacial/interglacial period. The mid-Holocene low atmospheric CH_4 concentrations might be mainly due to a reduction in tropical CH_4 sources (i.e., drying of the tropics, Flückiger et al. 2002), while the subsequent increase has been attributed to an expansion of boreal wetlands, although this has yet to be substantiated. It has also been suggested that the increase in atmospheric CH_4 concentration between 5000 and preindustrial period were the result of early agricultural activities in Eurasia, particularly forest clearance and rice cultivation (Ruddiman 2003). However, this early anthropogenic emissions hypothesis has been criticized and undergone significant modifications (Claussen et al. 2005; Broecker and Stocker 2006; Masson-Delmotte et al. 2006; Ruddiman 2007). It generally accepted that the reasons for late Holocene trends in CH_4 concentration is still not available (Wolff and Spahni 2007) due to findings that $\delta^{13}CH_4$ declined significantly from 1000 to 1800 AD (Fig. 7.3b) in absence of major changes in CH_4 concentrations (Ferretti et al. 2005).

Several mechanisms have been proposed to explain the late Holocene increase in atmospheric CH_4, including: (i) expansion of boreal wetland source areas (Blunier et al. 1995; Velichko et al. 1998), (ii) the CH_4 emission responses to changing climate (Indermuhle et al. 1999), and (iii) agricultural development, particularly rice paddy cultivation and widespread domestication of ruminants (Chappellaz et al. 1997; Ruddiman 2007). However, model simulations have not been able to simulate the anthropogenic or natural influence of CH_4 increase in the late Holocene. Part of the late Holocene CH_4 concentration increase could be anthropogenic (Kaplan et al. 2006) and part could be natural. However, natural wetland CH_4 models driven by simulated climate changes are able (Singarayer et al. 2011) or unable (Konijnendijk et al. 2011) to simulate the increase in CH_4 concentration observed in ice cores, reflecting the climate sensitivity of the modern CH_4 emissions from wetlands simulated by the models (Melton et al. 2013). The variations observed in CH_4 and $\delta^{13}CH_4$, are somewhat dissimilar (Fig. 7.3a, b) compared to those observed in CO_2 and $\delta^{13}CO_2$ during Holocene. Moreover, significant changes in atmospheric CH_4 can be caused by changes in specific sources and sinks that do not necessarily require the larger translocations of C needed to change atmospheric CH_4 and $\delta^{13}CH_4$, since CH_4 concentrations tends to be more susceptible to rapid

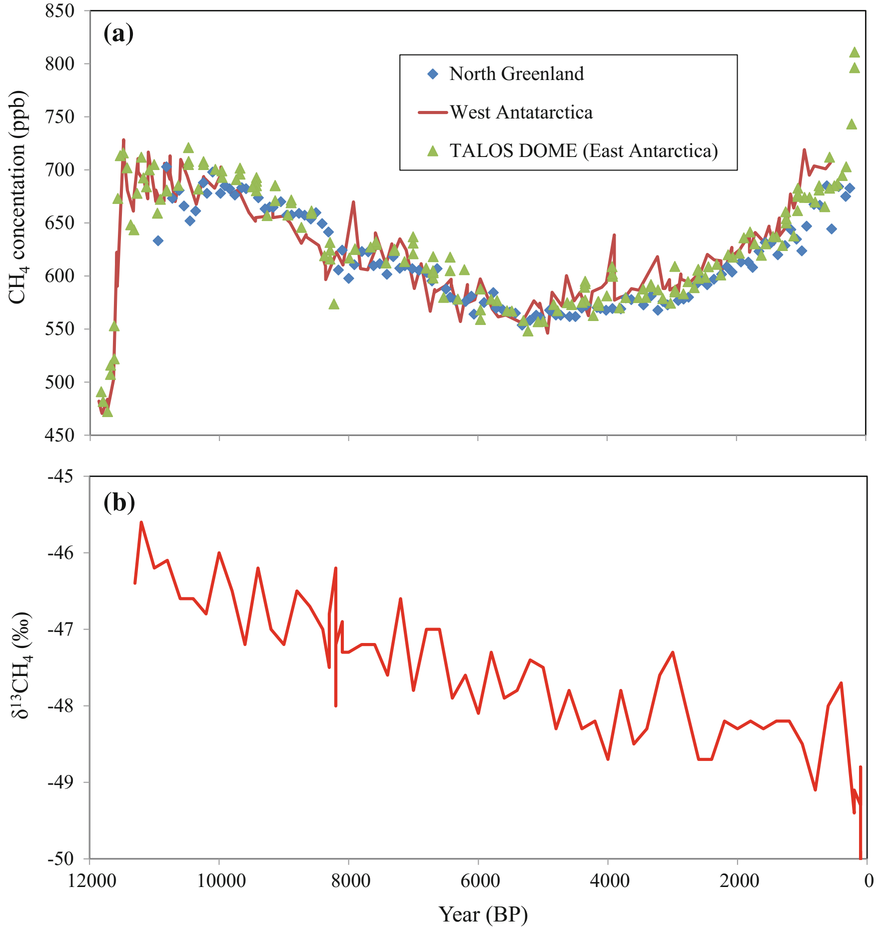

Fig. 7.3 The methane concentration and $\delta^{13}CH_4$ record covering the Holocene period. *Source* Sowers (2010), Blunier et al. (1995), Brook et al. (1996, 2000), Buiron et al. (2011). Data available at https://www.ncdc.noaa.gov

variations resulting from changes in sources than CO_2 (Sundquist and Ackerman 2014). As a result, abrupt changes and spikes are generally more common in ice core records of CH_4 concentration than that of CO_2, which can be important links between climate and C cycle changes. Therefore, it is likely that a variety of processes reflecting the regional and global complexity of both C cycling and the climate contributed to the trends recorded in ice cores of the Holocene period CH_4. The atmospheric CH_4 concentration are more susceptible to rapid variations resulting from changes in sources than CO_2 concentrations, as the abrupt changes and spikes in CH_4 concentration record indicates.

The dominant source of natural CH_4 are wetlands which mainly occur in the tropics and northern hemisphere. The CH_4 produced in northern hemisphere is oxidized during its transit southward in the atmosphere, resulting in north to south decreasing atmospheric CH_4 concentration. This gradient appears to have varied during the recent millennium, with the CH_4 concentrations over Greenland exceeding those from Antarctica by 24 to 58 ± 10 ppb (Etheridge et al. 1998). The CH_4 measurements in ice from Law Dome site in Antarctica reveals a small variation that parallel the CO_2 trends over the last millennium. The CH_4 decrease by ~40 ppb in 16th and 17th century (Fig. 7.4; Etheridge et al. 1998; MacFarling Meure et al. 2006; Mitchell et al. 2011). Lower temperatures during this period may have reduced CH_4 emissions by wetlands. Alternative explanations that have been suggested include: (i) changes in biomass burning (Mischler et al. 2009), and (ii) changes in CH_4 emissions as a result of wars and plague (Mitchell et al. 2011). However, the $\delta^{13}CH_4$ measurements suggest pronounced variability in both anthropogenic and natural atmospheric CH_4 sources between 1000 and 1800 year-period (Ferretti et al. 2005; Sapart et al. 2012). Analysis of $\delta^{13}CH_4$ from Greenland ice cores and application of two-box model attributed the centennial variations in $\delta^{13}CH_4$ between 100 AD and 1600 AD to changes in pyrogenic and biogenic sources driven by both natural climate variability and changes in human population and land use (Ferretti et al. 2005; Sapart et al. 2012). Therefore, on the basis of $\delta^{13}C$ isotope, the pre-industrial CH_4 sources can be divided into three categories: biogenic CH_4 (e.g., wetlands, rice paddies, and ruminants, mean

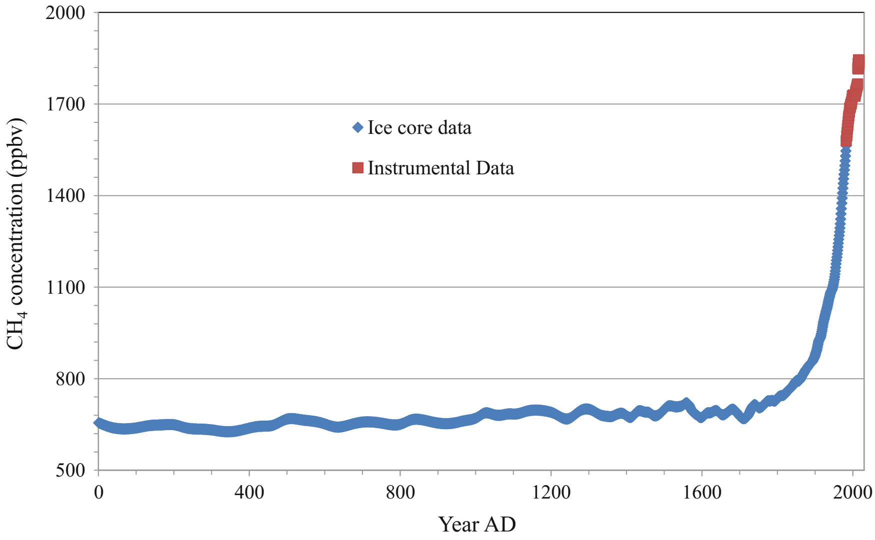

Fig. 7.4 Law Dome ice core CH_4 concentrations over the last 2000 years superimposed by modern instrumental atmospheric CH_4 measurements (Etheridge et al. 1998; MacFarling Meure et al. 2006). Data available at https://www.ncdc.noaa.gov

$\delta^{13}CH_4 = -60 \pm 5‰$), geological CH_4 (e.g., mud volcanoes, and micro-seepages, mean $\delta^{13}CH_4 = -38 \pm 7‰$), and pyrogenic CH_4 (e.g., fires, biofuel, and coal burning, mean $\delta^{13}CH_4 = -22 \pm 3‰$) (Quay et al. 1999; Ferretti et al. 200; Mischler et al. 2009; Houweling et al. 2008). Significant $\delta^{13}CH_4$ depletion during the last millennium (1000–1800) has been observed, which was attributed to changes in biomass burning emissions, probably influenced by both human activities and natural climate change (Ferretti et al. 2005). After 1800, an abrupt isotopic enrichment is observed, presumably resulting from increased fossil fuel emissions associated with the onset of industrialization (Ferretti et al. 2005; Mischler et al. 2009; Houweling et al. 2008).

7.2.3 Methane Concentration During the Industrial Era

The atmospheric CH_4 concentrations of the Industrial Era (i.e., after 1750) have been determined through reconstruction using air trapped in polar ice cores and firn air, the measurement record which has extended to recent decades (Etheridge et al. 1998; Ferretti et al. 2005; MacFarling Meure et al. 2006; Sapart et al. 2013). Measurements of CH_4 concentration from ice cores of Antarctica and Greenland suggest that after a very slow atmospheric CH_4 concentration increase averaged at 0.04 ppbv yr^{-1} during the pre-industrial times from 1 to 1750, the atmospheric CH_4 concentration increased rapidly at an average rate of about 4.0 ppb yr^{-1} during industrial times from 1750 to 1990 (Rasmussen and Khalil 1984; MacFarling Meure et al. 2006; Etheridge et al. 1998). Globally averaged atmospheric CH_4 concentration in 1750 was 722 ± 4 ppbv (Dlugokencky et al. 2005). After 1750, the atmospheric CH_4 levels rose gradually and reached 830 ppb by about 1850, then it increased exponentially with time reaching 1650 ppb by mid-1980s (Fig. 7.4; Etheridge et al. 1998). The global atmospheric abundance in 2015 is 1845 ± 2 ppb (WMO 2016). The extrapolated CH_4 trends from ice cores to the time periods with direct instrumental measurements are consistent with recent atmospheric measurements (Fig. 7.4; Stauffer et al. 1985; Etheridge et al. 1992), and provides a powerful support for the validity of ice core records extending back in time.

Direct measurements of CH_4 in the atmosphere at high precision began in 1978 (Blake et al. 1982; Rasmussen and Khalil 1984; Etheridge et al. 1992) and reached global coverage after 1983. Currently, the atmospheric CH_4 concentration is measured by a network of more than 100 discrete surface air samples collected regularly and with continuous measurements made at the surface (Etheridge et al. 1992; Blake et al. 1982; Francey et al. 1999; Cunnold et al. 2002; Dlugokencky et al. 2009, 2011), or in the troposphere profiles by aircraft (Brenninkmeijer et al. 2007), satellite (Wecht et al. 2012; Schuck et al. 2012), and remotely sensed measurements of atmospheric CH_4 columns retrieved from the surface or from space (Crevoisier et al. 2009; Frankenberg et al. 2011; Morino et al. 2011). Surface based observations from four networks—National Oceanic and Atmospheric Organization (NOAA), Advanced Global Atmospheric Gases Experiment (AGAGE), Commonwealth Scientific and Industrial Research Organization (CSIRO), University of California Irvin (UCI) have shown consistent changes in global growth rate of annual CH_4 concentrations since 1980s. Between the mid-1980s and 2000s the atmospheric growth rate of CH_4 declined from an average of 12 ± 6 ppb yr^{-1} in 1980s to 6 ± 8 ppb yr^{-1} in 1990s, and a general stabilization at nearly zero and concentration of 1773 ± 3 ppb from 1999 to 2006, a quasi-stable concentration, where the sum of emissions are in balance with the sum of sinks (Fig. 7.5; Dlugokencky et al. 2003; Khalil et al. 2007; Patra et al. 2011; Alexe et al. 2015). The atmospheric CH_4 increase picked up again from 2007 (Rigby et al. 2008). Since 2007, the atmospheric CH_4 concentrations have been increasing again at nearly steady state of ~6 ppb yr^{-1} (Fig. 7.5, Rigby et al. 2008; Dlugokencky et al. 2009), and reached 1845 ± 2 ppb in 2015 (WMO 2016). The atmospheric CH_4 concentrations have increased by 2.53 times compared to pre-industrial concentrations of 722 ± 4 ppb (after conversion to NOAA 2004 standard scale (Dlugokencky et al. 2005). This increase reflects recent imbalance between CH_4 sources and sinks that is not fully understood (Dlugokencky et al. 2011), but is probably related to increased emissions from wetlands as a feedbacks from global climate change (Hoehler and Alperin 2014; Yvon-Durocher et al. 2014). There is very high level of confidence that anthropogenic activities caused

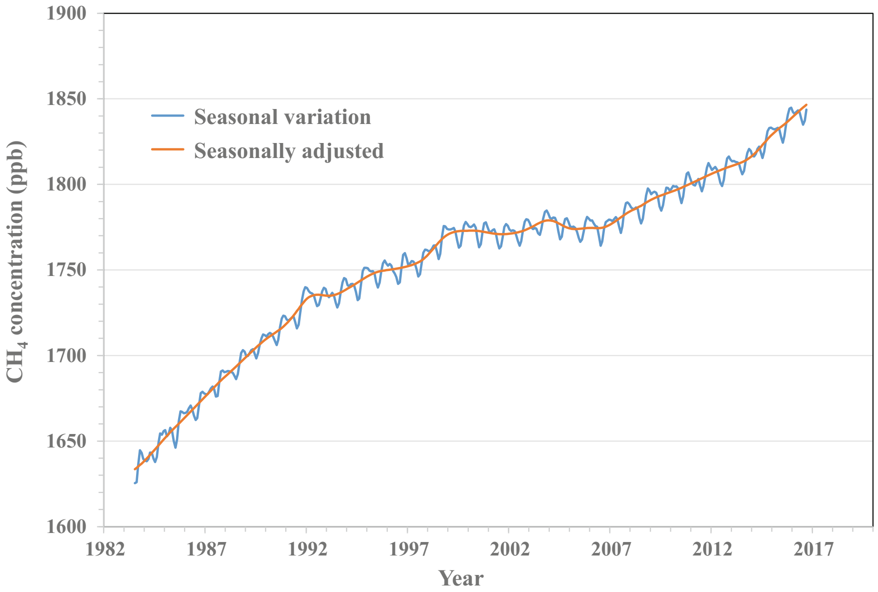

Fig. 7.5 The atmospheric CH_4 mole fraction for the period 1983 to 2014 averaged from NOAA data (available online at: ftp://aftp.cmdl.noaa.gov/data/trace_gases/)

the increase in atmospheric CH_4 concentration during the industrial era (Ciais et al. 2013). There are indications of increased anthropogenic and wetland emissions (Dlugokencky et al. 2009; Bousquet et al. 2011), but relative changes in anthropogenic and wetland emissions remains uncertain (Kirschke et al. 2013). Overall, the Arctic CH_4 concentration increased more than the global growth rate in 2007, but since then the Arctic growth rate has tracked the global growth rate, but in the southern tropics, the growth rate has remained above the global trends since 2007 (Nisbet et al. 2014).

The reasons for the atmospheric CH_4 growth rate decline after the mid-1980s and the eventual stabilization from 1999 to 2006 are still debated but several scenarios quoted include: (i) reduction of anthropogenic emitting activities—including fossil-related emissions (coal mining, oil, and gas industry) estimated from AGAGE and NOAA data (Chen and Prinn 2006) or from ethane used as a proxy to fossil fuel-related CH_4 emissions (Aydin et al. 2011) and animal husbandry, especially in the countries of the former Soviet Union (Savolainen et al. 2009; Simpson et al. 2012), (ii) a compensation between increasing anthropogenic emissions and decreasing wetland emissions (Chen and Prinn 2006; Bousquet et al. 2006), (iii) significant to small changes in atmospheric hydroxyl ions (OH) concentration based on $^{13}CH_4$ datasets (Rigby et al. 2008; Montzka et al. 2011), (iv) reduced emissions from rice paddies attributed to changes in agricultural practices for paddy rice production such as water regime management (Kai et al. 2011), or (v) stable microbial and fossil fuel emissions from 1990 to 2005 (Levin et al. 2012). A synthesis of data suggests that a stable to increasing microbial emissions and a stable to decreasing fossil fuels emissions is more likely than other scenarios to explain the observed stability but it did not attribute those changes regionally (Kirschke et al. 2013).

The global network of instrumental measurements of CH_4 have improved the knowledge of CH_4 concentration in the atmosphere. The measured concentrations in the atmosphere are used to improve the CH_4 sources estimate both at country and regional level. Measurements from the global network of air sampling are also used in simulations of global atmospheric CH_4 chemistry and transport. Globally averaged monthly CH_4 mol fraction for surface flask measurements from NOAA/ESRL network indicates that atmospheric CH_4 concentration is the highest at the end of winter and decreases to the minimum during summer (Fig. 7.5) due to CH_4 oxidation in summer. The atmospheric CH_4 concentration increase since 1750 implies an anthropogenic emission of 340 ± 50 Tg CH_4 yr^{-1}. The concentration is higher than ever observed in ice core record over the past 800,000 years (Loulergue et al. 2008b).

The causes of renewed growth in atmospheric CH_4 burden since 2007 are still poorly understood and subject of intensive scientific discussion (Dlugokencky et al. 2009, 2011; Rigby et al. 2008). Recent studies have attributed the increased emissions of CH_4 in the Arctic as a result of higher temperatures in 2007 and greater rainfall in the tropics in 2008 (Dlugokencky et al. 2009). The temperature response is a snapshot of potentially positive feedback, with higher temperatures projected at high latitudes for the 21st century, increasing CH_4 emissions from wetlands, permafrost, and possibly CH_4 hydrates. Derived global CH_4 emissions for 2007–2010 estimated by top-down inverse modeling using climatological OH fields are 16–20 Tg CH_4 yr^{-1} higher compared to 2003–2005 estimates, with most of inferred emission increase occurring in tropics and mid-latitudes of northern hemisphere (Bergamaschi et al. 2013).

7.3 Global Methane Budget

The global CH_4 budgets are overviews of sources and sinks of CH_4 derived from a priori emission estimates and long-term measurements of CH_4 concentrations at some background stations. The global CH_4 sources and sinks estimates are presented in Table 7.1. The global network of CH_4 measurement instruments have improved the knowledge on CH_4 concentrations in the atmosphere and the measured CH_4 concentrations are used to improve the understanding of source estimates at country, regional, and global level. The measurements from global air sampling network are also used in simulations of the global atmospheric chemistry and transport. Satellite information from monitoring instruments can also be used to validate model simulations and develop global maps of emission estimates. Inverse modeling which uses top-down approach to model the emission sources is also used to improve the priori emission estimates. For example, emission estimates from tropical wetlands and remote areas were improved through inverse modeling using satellite data (Bergamaschi et al. 2005, 2007, 2009, 2013; Alexe et al. 2015). Atmospheric CH_4 contribution to anthropogenic climate forcing is about half that from CO_2 when direct and indirect components of its forcing are summed (Hansen and Sato 2001). Therefore, better understanding of the global CH_4 budget and how it is changing with time is important for targeting specific sources for reduced CH_4 emission and mitigating future environmental impacts.

The atmospheric CH_4 growth rate results from the imbalance between CH_4 emissions and CH_4 sinks. Increase in atmospheric CH_4 during the industrial era is driven mostly by anthropogenic CH_4 emissions from fossil fuels, industry, agricultural activities, biomass burning and waste. However, there are indications that meteorological feedbacks from changing climate may have also played a role by changing natural CH_4 emissions (Dlugokencky et al. 2011). Both paleorecords and current studies suggest that some sources of emissions such as wetlands and CH_4 hydrates, may be subject to strong positive feedbacks on warming (Nisbet and Chappellaz 2009). Therefore, targeting CH_4 emission is important strategy in efforts to mitigate climate change, and understanding the CH_4 budgets plays significant role in developing mitigation strategies. Global CH_4 budgets are generally quantified overview of sources and sinks for CH_4. They are a priori emission estimates and long-term measurements of CH_4 at background stations.

Table 7.1 Estimated Global of CH_4 sources and sinks for three decades of instrumental measurement (1980–2009)

Sources	CH_4 flux (Tg CH_4 yr^{-1})					
Decade	1980–1989		1990–1999		2000–2009	
	Top-down	Bottom-up	Top-down	Bottom-up	Top-down	Bottom-up
Natural sources	150–267	183–466	144–197	179–465	142–273	177–484
Natural wetlands	115–231	183–266	144–160	169–265	142–208	177–284
Other sources	35–36	61–200	23–37	61–200	37–65	61–200
Freshwater		61–200		8–73		8–73
Wild animals		15		15		15
Wildfires		1–5		1–5		1–5
Termites		2–22		2–22		2–22
Geological		33–75		33–75		33–75
Hydrates		2–9		2–9		2–9
Permafrost		0–1		0–1		0–1
Other sources	35–36	61–200	23–37	61–200	37–65	61–200
Total natural	150–267	244–466	167–197	230–465	179–273	238–484
Anthropogenic sources	305–383	292–323	290–453	281–347	273–409	304–368
Agriculture and waste	187–220	172–197	180–301	177–196	180–241	187–224
Ruminants		81–90		82–91		87–94
Rice		41–47		32–37		33–40
Landfills and waste		50–60		63–68		67–90
Biomass burning	43–55	31–37	38–45	38–45	2445	32–39
Fossil fuels	75–104	89	84–107	66–96	77–123	85–105
Sinks						
Total chemical loss	450–533	411–671	491–554	521–621	510–538	483–738
Tropospheric OH		382–567		457–501		454–617

(continued)

Table 7.1 (continued)

Sources	CH_4 flux (Tg CH_4 yr^{-1})					
Decade	1980–1989		1990–1999		2000–2009	
	Top-down	Bottom-up	Top-down	Bottom-up	Top-down	Bottom-up
Stratospheric OH		16–67		51–83		16–84
Tropospheric Cl		13–37		13–37		13–37
Soils	10–27	9–47	27	9–47	26–42	9–47
Sum of sources	500–592	536–789	529–596	511–812	526–569	542–852
Sum of sinks	460–559	420–718	518–579	530–668	514–560	592–785
Imbalance	16–40		7–17		4–19	
Atmospheric growth	34		17		6	

7.3.1 Methane Sources

CH_4 is emitted into the atmosphere by both natural and anthropogenic sources. Natural sources include wetlands, oceans, hydrates, geological sources, wild ruminant animals, termites, and wild fires. Important anthropogenic sources include coal mining, gas and oil industry, landfill and waste, domesticated ruminants, rice agriculture, and biomass burning. Natural sources are currently outweighed by anthropogenic sources. For example, decadal natural and anthropogenic CH_4 emissions estimated by bottom-up approach for 2000s are 347 ± 109 and 331 ± 27 Pg CH_4 yr^{-1}, respectively (Table 1, Kirschke et al. 2013; Ciais et al. 2013). Many significant sources of CH_4 on global scale, both natural and anthropogenic methanogenesis, except biomass burning, geological and fossil fuel sources.

Sources of CH_4 emissions can be broadly grouped into three categories: biogenic, thermogenic, and pyrogenic origin (Neef et al. 2010), and they can be the direct result of either anthropogenic activities and/or natural processes. Biogenic sources contain CH_4-generating microorganisms (i.e., methanogens), where CH_4 is generated from degradation of organic matter in anaerobic conditions (Cicerone and Oremland 1988). Such sources comprise natural wetlands and rice paddies, oxygen-poor fresh water reservoirs such as dams, digestive systems of ruminants and termites, and organic waste deposits such as manure, sewage, and landfills. Thermogenic CH_4 consists of CH_4 formed over millions of years through geological sources as a result of slow transformation of organic matter into fossil fuel. It can be vented from subsurface into the atmosphere through natural features such as terrestrial seeps, marine seeps, and mud volcanoes. It is also vented to the atmosphere through anthropogenic activities of exploitation of coal, oil, and natural gas. Pyrogenic CH_4 is produced by incomplete combustion of biomass, soil organic carbon (SOC), and other organic materials during wild fires, combustion of biofuels, and combustions of fossil fuels. Each of these three sources of CH_4 are characterized by ranges of isotopic $\delta^{13}C$ composition of CH_4, typically $\delta^{13}CH_4$ range of −55 to −70‰ for biogenic emissions, −25 to −45‰ for thermogenic emissions, and −13 to −25‰ for pyrogenic emissions (Bousquet et al. 2006; Monteil et al. 2011; Neef et al. 2010). The isotopic composition of atmospheric CH_4 measured at subset of surface atmospheric monitoring stations has been used to constrain the atmospheric CH_4 source (Neef et al. 2010; Bousquet et al. 2006; Monteil et al. 2011; Fisher et al. 2011). The CH_4 emissions by living plants under aerobic conditions seems to play less significant role in global CH_4 budgets, contrary to very large estimates which have been reported (Keppler et al. 2006; Nisbet et al. 2009).

Since large-scale global or regional CH_4 fluxes cannot be directly measured, the estimation of these quantities are generally obtained through two complementary techniques—“bottom-up” emission inventories and “top-down” inverse modeling (Alexe et al. 2015). Top-down Bayesian inverse modeling approach operates under well-defined mathematical framework which combines a priori information on CH_4

Table 7.2 Estimated top-down CH_4 budget for year 2011

Source	Methane pool
Global atmospheric burden (Tg CH_4)	4954 ± 10
Annual atmospheric loss (Tg CH_4 yr^{-1})	542 ± 56
Atmospheric increase (Tg CH_4 yr^{-1})	14 ± 3
Natural sources (Tg CH_4 yr^{-1})	202 ± 35
Anthropogenic sources (Tg CH_4 yr^{-1})	354 ± 45
Total source (Tg CH_4 yr^{-1})	556 ± 56

emissions, atmospheric observations, atmospheric chemistry, and transport models to determine optimal surface fluxes that best fit the atmospheric CH_4 concentration observation over the period of interest (Kasibhatla et al. 2000), given the prior fluxes and their uncertainties. In this approach, the global concentration fields are used as input to estimate the sources and sinks. The results of inverse modeling are called 'a posteriori' or improved estimates (Van Amstel 2012).

The top-down estimates are generally those of regional emissions derived from global atmospheric concentration fields, are not easily interpreted, and are difficult to assign into individual sources. The quality of estimates obtained through inverse modeling depends in most part on the quality of the observational data available for spatial and temporal domain of interest, and on the quality of chemistry and transport models, however. The global atmospheric inversions provide a time varying distribution of CH_4 fluxes with limited insight into underlying biogeochemical processes controlling the emissions, especially where several processes and different sources overlap in the same region (Kirschke et al. 2013). The global to-down CH_4 estimates for 2011 are presented in Table 7.2.

The decadal global top-down CH_4 emissions modeled based on the observation of the global CH_4 burden and estimate of its atmospheric lifetime of ~9.1 years for 1980s, 1990s, and 2000s are estimated at 551 ± 41, 554 ± 42, and 548 ± 21 Tg CH_4 yr^{-1}, respectively, of which, the global anthropogenic burden was 34,843, 37,282, and 33,562 Tg CH_4 yr^{-1} for 1980s, 1990s, and 2000s, respectively (Kirschke et al. 2013; Ciais et al. 2013). The estimated atmospheric CH_4 growth rate by inverse models for 1980s, 1990s, and 2000s were 34, 17, and 6 Tg CH_4 yr^{-1} (Kirschke et al. 2013). The two-year average emissions for 2010 and 2011 estimated by four top-down models is 538.4 Tg CH_4 yr^{-1} (Alexe et al. 2015). However, models did not aggregate the emissions into natural and anthropogenic sources.

The bottom-up approach incorporate the knowledge of small-scale processes, and with additional information and constraints it can project local emissions to large scales compatible with atmospheric signals. The approach includes process based models estimating CH_4 emissions and chemistry climate models estimating the OH sink. Bottom-up emission inventories based on energy use, agriculture activities, and emission factors from different sectors are used to provide yearly or decadal mean estimates of anthropogenic emissions. The decadal bottom-up CH_4 emissions, (i.e., sum of natural and anthropogenic sources) for 1980s, 1990s, and 2000s are 663 ± 127, 699 ± 138, and 678 ± 136 Tg CH_4 yr^{-1}, respectively

(Table 1, Kirschke et al. 2013; Ciais et al. 2013). Global CH_4 burden derived from bottom-up approach are generally much larger than those obtained from top-down estimates.

7.3.1.1 Overview of Inventories of Methane

The global sources of CH_4 is composed of wide range of sources, balanced by much smaller number of sinks, and any imbalance in these sources and sinks results in change in the atmospheric CH_4 concentration. Of the many significant sources of CH_4 on a global scale, both natural and anthropogenic, the bulk have a common basis—that of microbial methanogenesis. Although CH_4 from biomass burning, vegetation, and geological or fossil fuel sources may be largely non-microbial in nature, understanding the processes that underpin microbially mediated CH_4 fluxes is central to quantifying and, potentially reducing emissions from all major sources. The current understanding of microbial methanogenesis and the interactions between different microbial communities that result in the bulk of CH_4 emissions to the global atmosphere is discussed in the following section.

Natural Methane Sources

The major natural CH_4 sources include wetlands, termites, and release from onshore and offshore geological sources. Living vegetation has also been suggested as an important natural source of CH_4 (Keppler et al. 2006). However, the significance of aerobic plant sources have been questioned, and the earlier emission estimates have been significantly revised downwards (Kirschbaum et al. 2006; Parsons et al. 2006).

Wetlands

In wetlands, CH_4 is formed under anaerobic conditions by microbial decomposition of OM. The CH_4 production occurs under anaerobic soil conditions in natural wetlands as well as in rice paddies. The CH_4 is formed by methanogenic organisms. It is estimated that 2–7% of the net primary productivity (NPP) in wetlands is emitted as CH_4 (Aselmann and Crutzen 1989). The three key determinants of CH_4 emission from wetlands are: (i) temperature (Christensen et al. 2003), (ii) water table depth (Macdonald et al. 1998), and (iii) substrate availability (Christensen et al. 2003). The degree of sensitivity of emissions to changes in these determinants remains poorly resolved. Generally temperature tends to be the dominant factor. For example, in a number of northern wetland sites, soil temperature variation accounted for 84% of observed variation in CH_4 emissions with strong positive response to increased temperature (Christensen et al. 2003). Emissions from Arctic, in particular, have the potential to increase significantly as the global temperature increases and the vast stores of SOC thaw (Schuur et al. 2011; Harden et al. 2012).

Therefore, the impact of climate change on CH_4 emissions from natural wetlands in the 21st century could be substantial. It has been suggested that an increase in global temperature by 3.4 °C could result in a 78% increase in wetland CH_4 emissions, which will amplify total anthropogenic radiative forcing by between 3.5 and 5% by 2100 (Shindell et al. 2004). Decadal emissions from natural wetlands estimated by bottom-up for 1880s, 1990s, and 2000s ranged from 183 to 266, 169 to 265, and 177–284 Tg CH_4 yr^{-1}, respectively, accounting for 57–75% of natural CH_4 emissions. The decadal emissions for the same period estimated by top-down inverse modeling ranged from 115 to 231, 144 to 160, and 142 to 208 Tg CH_4 yr^{-1}, respectively (Table 1, Kirschke et al. 2013; Ciais et al. 2013), reflecting increasing emission trends from global natural wetlands.

Geological Methane

The natural CH_4 emissions from geological sources have often focused on CH_4 hydrates, also called clathrates (i.e., ice-like mixtures of CH_4 and water found in ocean sediments). The CH_4 clathrates, discussed further in the following section. Because these hydrates have potential of climatic warming, destabilizing them has received significant attention in recent years (Westbrook et al. 2009). Etiope (2012) opined that the estimates of emissions from hydrates remains highly speculative, and that the overall geological sources of CH_4 emission to the atmosphere is higher than is commonly reported. In addition to emissions from CH_4 hydrates, CH_4 emissions also occurs through sedimentary seepage, mud volcanoes, other macro- and micro-seeps, geothermal and volcanic emissions. It is estimated that natural geological emissions could be responsible for as much as 33–80 Tg CH_4 yr^{-1}, (Etiope 2010; Kirschke et al. 2013; Ciais et al. 2013), and has remained constant over the last three decades. The determinants of geological CH_4 emissions include seismic activity, tectonics, and magmatism. Therefore, the global atmospheric CH_4 budget is also influenced by geophysical processes (Etiope 2010). Hydrate CH_4 is a potential sources of natural gas, but the method for its exploitation has not been established. Estimated of CH_4 emissions from hydrates range from 2 to 10 Tg CH_4 yr^{-1} (Ciais et al. 2013; Westbrook et al. 2009), and overall emissions are increasing at an alarming rate (Westbrook et al. 2009).

CH_4 emissions from thawing permafrost and CH_4 hydrates in the northern circumpolar region will become potentially important in the 21st century because they could increase dramatically due to the rapid climate warming of the Arctic and the large C pools stored there (Tarnocai et al. 2009; Walter Anthony et al. 2012). Supersaturation of dissolved CH_4 at the bottom and surface waters in the East Siberian Arctic Shelf indicate some CH_4 activity across the region, with a net sea–air CH_4 flux of 10.5 Tg CH_4 yr^{-1}, which is similar in magnitude to that for the entire ocean (Shakhova et al. 2010). However, it is not possible to know whether these fluxes are the result of recent changes in Arctic or it has always been present. The ebullition of CH_4 from thawing and decomposing lake sediments in north Siberia with an estimated flux of $\sim$4 Tg CH_4 yr^{-1} also demonstrates the activity of this region, and of its potential importance in the future CH_4 emissions (Walter et al. 2006; van Huissteden et al. 2011; Walter Anthony et al. 2012).

Other natural sources of CH_4 include termite, freshwater and lakes, wild animals, permafrost, wild fires and vegetation. Some termite species produce no CH_4 at all. But the emission rarely exceed half a microgram per termite per day for those that do. However, the shear mass of termites globally gives rise to considerable estimate in global budget. With improved measurements and understanding of differences in CH_4 production rates between different termite species, and issues associated with upscaling and effects of land use change, that the importance of termites as a global source of CH_4 is probably overstated (Bignell 2010).

The CH_4 emissions from biomass burning are the result of incomplete combustion, and it encompasses a wide range of sources, including fuel wood, charcoal, peat, savannah, agricultural residues, agricultural waste and municipal waste combustion. Higher CH_4 emissions from biomass burning generally occur at high water content and low O_2. In developing countries, biomass burning is common energy source for heating, cooking and lighting purposes. Differentiating between natural and anthropogenic CH_4 source is inherently difficult, however. The IPCC Assessment Report (AR5) estimated that emissions from wild fires remained constant from 1980s to 2000s at 1–5 Pg CH_4 yr^{-1}, while those from biomass burning increased from 31 to 37 Tg CH_4 yr^{-1} in 1980s, and to 32–39 Tg CH_4 yr^{-1} in 2000s (Ciais et al. 2013). During the decade of 2000s, the natural CH_4 sources are estimated to account for 35–50% of the decadal global mean CH_4 emissions with the wetlands being the dominant source. The climate-driven changes in emissions from wetlands are the main drivers of the global inter-annual variability in CH_4 emissions. The sum of all natural emission estimates other than wetlands is still uncertain based on bottom-up studies and range of 238–484 Tg CH_4 yr^{-1} for 2000–2009 (Kirschke et al. 2013; Ciais et al. 2013).

Anthropogenic Methane Sources

The anthropogenic emissions of CH_4 ranged between 50 and 65% of the global emissions since 2000s (Ciais et al. 2013), and the anthropogenic sources of CH_4 emissions can be grouped by sector into (i) agriculture, (ii) energy, (iii) waste, and (iv) industry. Figure 7.6 shows contribution of each sector to total anthropogenic CH_4 emission.

Agriculture

Agricultural sector is the largest contributor to global emissions of non-CO_2 GHG emissions, accounting for about 51% of anthropogenic CH_4 emissions (Fig. 7.6). The dominant source of agricultural CH_4 emission is the enteric fermentation which constitute nearly 60% of agricultural emissions, followed by emissions from rice cultivation, other agricultural activities, and manure management. China is the

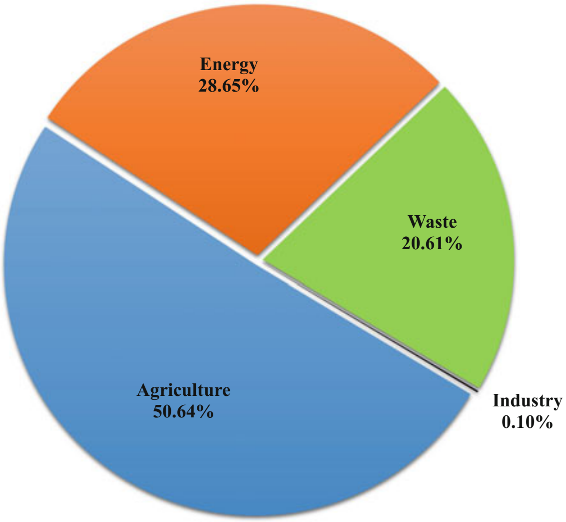

Fig. 7.6 Contribution of different sectors to anthropogenic CH_4 emissions calculated based on average emissions from 1990 to 2010

largest agricultural emission source, constituting 15.45% of global agricultural emissions. Other significant emitters are India, Brazil, and USA, among others. The top 10 emitters are responsible for 55% of agricultural emissions (Karakurt et al. 2012).

Enteric Fermentation

About 90% of annual anthropogenic CH_4 emissions in rural communities is due to rumen fermentation (Abberton et al. 2008). The enteric fermentation represents about 80% of CH_4 emission produced by livestock, but the emissions vary over time and between different regions of the world. The CH_4 is formed by methanogenic bacteria under anaerobic conditions in the rumen of domestic animals, a process which enables these animals to utilize the energy more efficiently from low-quality feeds like grass and fodder with high cellulose content. Pseudo-ruminants like horses and pigs also produces CH_4, but in much smaller quantities. Rumen methanogenesis results in the loss of 6–10% of gross energy intake or 8–14% of digestible energy intake of ruminants (Cottle et al. 2011). The bulk (>90%) of CH_4 produced in rumen is emitted through belching, and some dairy cattle emit several hundred liters of CH_4 per day. The CH_4 emissions produced by domestic ruminants depend on the feeding intake, energy consumption, rumen condition, and digestibility. The CH_4 emissions from ruminant livestock are highly dependent on demand pressure, and the global trend of increasing consumption of meat and dairy products with increased CH_4 emissions. In 2005, CH_4 emissions from ruminant livestock were estimated at 72 Tg CH_4 yr^{-1}, and projected to be as high as 100 Tg CH_4 yr^{-1} in 2010 (Kelliher and Clark 2010).

The IPCC AR5 estimated decadal changes in ruminant CH_4 emission for 1980s, 1990s, and 2000s at 81–90, 82–91, and 87–94 Tg CH_4 yr^{-1}, respectively (Ciais et al. 2013). CH_4 emissions from enteric fermentation are projected to increase by 22% by 2030, mostly due to increases in livestock production. The largest increases in CH_4 emission is expected to occur in Africa and Asia (EPA 2012).

Manure

CH_4 from animal manure is formed in anaerobic conditions when stored in lagoons or in manure tanks. Microbial methanogenesis in manure has the potential to produce significant amount of CH_4 because of high availability of OC substrates and anoxic conditions that tend to prevail. However, when manure is kept in contact with O_2 (i.e, spread on the fields), the CH_4 production is minimal. The quantity of CH_4 emitted from manure management operations is a function of three primary factors: (i) type of treatment or storage facility, (ii) the ambient climate, and (iii) the composition of manure. Higher ambient temperature and moisture conditions favor CH_4 production. The composition of manure is directly related to animal type and diet. Therefore, manure management system has significant influence on CH_4 emission.

Rice Paddies

CH_4 is formed by methanogenic organisms in flooded paddy soils during a growing season, escapes through bubbling and diffusion, and rice stems. Draining of the fields stops CH_4 formation due to aeration. Globally, about 80 million ha (Mha) of harvested wetland rice are potential sources of CH_4. Most paddies are submerged for about one third of the time, although practices vary widely around the world based on rice variety, culture, and water availability. The estimated emissions are 200–500 mg m^{-2} during an average rice growing season of 130 days. Rice is a staple food for many parts of the world, and with the population growth, the CH_4 emissions from rice cultivation are expected to increase. The IPCC AR5 estimated that the CH_4 emission from rice production decreased from 41–47 Tg CH_4 yr^{-1} in 1980s to 33–40 Tg CH_4 yr^{-1} in 2000s (Ciais et al. 2013). However, CH_4 emission from rice cultivation will increase only marginally by 2% between 2005 and 2030, mainly due to decrease in per capita consumption (EPA 2012) and improved water management regime.

Waste

Emissions from waste account for 21% of the anthropogenic emissions (Fig. 7.6). Major sources are waste water (41%) and landfilling solid waste (59%). The largest global emitter under this category is USA (13.8%), followed by China and India.

Waste Water Treatment

CH_4 is emitted from anaerobically treated human and industrial liquid wastes, mainly agribusiness. The potential amount of CH_4 formed in different treatment systems depend on characteristics like chemical and biological oxygen demand in the degradation and the storage time and temperature. Industrial waste water treatment such as food processing and pulp and paper facilities with high organic material loading tend to be the main contributors of CH_4 emissions. CH_4 is emitted incidentally or deliberately during handling and treatment of municipal wastewater. The organic material in wastewater produces CH_4 when it decomposes anaerobically (Talyan et al. 2007). Estimated CH_4 emissions from domestic waste are 29 Tg CH_4 yr^{-1} based on emission factor of 0.2–0.4 g CH_4 g^{-1} of chemical oxygen demand (Doorn et al. 2000). Global emissions from wastewater have increased by 35% between 1990 and 2005, and the main driver for the increasing domestic wastewater emissions is the population increase (EPA 2012).

Landfills

CH_4 is emitted from anaerobic decomposition of organic material in landfills. The O_2 trapped in the landfill is rapidly consumed by microorganisms in the closed landfill solid waste. CH_4 constituting about 50% of storage gas is produced as a result of anaerobic decomposition of organic materials in landfilling solid wastes. The major drivers of emission are the amount of organic material in landfills, the extent of anaerobic decomposition, the thickness as well as physical and chemical properties of the landfill cover material, the seasonal variation in CH_4 oxidation rate, and the level of landfill CH_4 collection and combustion—such as energy use or flaring (Themelis and Ulloa 2007; Lou and Nair 2009). Early estimates for landfill CH_4 emissions were as high as 70 Tg CH_4 yr^{-1}, but successful implementation of mitigation strategies and capture of CH_4 for beneficial energy use has seen the reduction in emission from landfills over the years (Borgner and Spokas 2010). Estimated decadal CH_4 Emissions from waste and landfills for 1980s, 1990s and 2000s were 50–60, 63–68, and 67–90 Tg CH_4 yr^{-1}, respectively (Ciais et al. 2013; Kirschke et al. 2013). Emissions from wastewater are projected to increase by 28% by 2030, with the highest increase occurring from Africa, Middle East, and Central and South America (EPA 2012).

Fossil Energy

CH_4 is the principal component of natural gas, accounting for 95% of pipeline quality gas. Much of the CH_4 emissions attributable to natural gas each year is derived from release during extraction, and processing, and distribution of natural gas. Oil production and processing upstream of oil refineries can also emit CH_4 in significant quantities since natural gas is often found in conjunction with petroleum deposits (Mitchell 1994). In both natural gas and oil production systems, CH_4 is a fugitive emission from leaking equipment, system fault, and deliberate flaring and venting at production field, oil refinery facilities, natural gas transmission line, compressor station leakage, natural gas storage facilities and natural gas distribution lines (Karakurt et al. 2012). Some CH_4 is also emitted during incomplete fossil fuel combustion. The amount of CH_4 released is related to combustion conditions and the content of the fuel (Karakurt et al. 2012).

Coal mining and extraction also release CH_4, and constitute one of the largest individual source activities of anthropogenic CH_4 emission. CH_4 is formed as a part of the geological process of coal formation, where large deposits of CH_4 can remain trapped within coal seams and surrounding rock strata and are liberated when pressure above or surrounding the coal bed is reduced as a result of natural erosion, faulting, or mining operations. Because CH_4 is explosive, it must be removed from underground mines high in CH_4 as a safety precaution. CH_4 concentrations between 5 and 15% in the air of coal mines represent an explosion hazard, and so ventilation is commonly employed to get rid of this CH_4.

The quantity of CH_4 emitted from mining operation is a function of coal rank and coal depth. Pressure increases with depth, and prevents CH_4 from migrating to the surface, and as a result, underground mining operations typically release more CH_4 than surface or opencast mining due to lower pressure and coal rank (EPA 1993). Coal rank and permeability, depth of coal seam, geologic parameters and the amount of production are among the factors affecting the quantity of CH_4 released (Karakurt et al. 2012). In addition, post mining processing of coal and abandoned mines also release CH_4. Between 1990 and 2005, global CH_4 emission from natural gas and oil systems are estimated to have increased by 21%, and from 2005 to 2030 by 31% (EPA 2012). Between 1990 and 2005, CH_4 emissions from coal mining are estimated to decrease by 2%, but projected to increase by 50% from 2005 to 2030 (EPA 2012). Based on top-down inversion models, decadal emissions from fossil fuels for 1980s, 1990s, and 2000s are estimated at 94.19 ± 19, 95 ± 11, and 96 ± 19 Tg CH_4 yr^{-1} respectively, while 89, 84 ± 18, and 96 ± 11 Tg CH_4 yr^{-1} have been estimated for the same period based on bottom-up approach (Kirschke et al. 2013). Some indications suggest that emissions from human activities such as intensification of hydraulic fracturing for the shale natural gas and oil extraction in USA and the global coal mining and especially Chinese and Indian economies have increased since 2007 (BP 2015; Karion et al. 2013; Ohara et al. 2007; Cooper et al. 2016). However, a full understanding of the hydraulic fracturing impact on GHG emissions require monitoring over the gas well lifetime and also analysis of transport distribution system. Some studies have indicated that increase in natural wetlands emission in response to high temperatures in northern high latitudes and increased rainfall over the tropical wetlands could be responsible for increase in emissions after 2006 (Bloom et al. 2010; Dlugokencky et al. 2011; Kirschke et al. 2013). Since 2007, atmosphere has become more depleted in ^{13}C an indication that the growth is dominated by ^{13}C richer wetland and ruminants emissions (NOAA 2015; Sherwood et al. 2016).

7.3.2 *Methane Sinks*

There are three sinks for CH_4 emitted to the atmosphere: (i) destruction of CH_4 by hydroxyl (OH) radicals in the troposphere and stratosphere, (ii) destruction by oxidizing bacteria (methanotrophs) in soils, and (iii) reactions with Cl in the troposphere and ocean surface. The primary sink for atmospheric CH_4 is the photochemical oxidation of CH_4 initiated by the reaction with OH radicals, mostly in the troposphere and stratosphere, which removes an amount equivalent to about 90% of the global CH_4 surface emission, and about 9% of the total atmospheric burden of 4700–4900 Tg CH_4 (Voulgarakis et al. 2013). The atmospheric lifetime of CH_4 with respect to OH and the atmospheric burden of 4800 Tg CH_4 is 7–11 years. Recent estimate of atmospheric CH_4 lifetime is 9.1 ± 0.9 years (Prather et al. 2012).

Additional oxidation sinks include methanotrophic bacteria in aerated soils which uses CH_4 as a source of C and energy (Curry 2007; Zhuang et al. 2004) which accounts for ~4% and reaction with chlorine radicals and atomic oxygen radical in the stratosphere (Cicerone and Oremland 1988; Neef et al. 2010; Nisbet et al. 2014) which oxidizes ~3%. A small sink of atmospheric CH_4 is also suspected but still debated, involves reactions with chlorine radicals from sea salt in the marine boundary layer (i.e., surface waters of the ocean) (Allan et al. 2007) estimated to oxidize ~3%. Decadal sink for atmospheric CH_4 for 1980s, 1990s and 2000s based on top-down atmospheric inversion models is estimated at 460–559, 518–579, and 514–560 Tg CH_4 yr^{-1}, respectively. The estimated decadal sink based on bottom-up for 1980s, 1990, and 2000s is 567 ± 147, 599 ± 69, and 632 ± 40 Tg CH_4 yr^{-1}, respectively (Table 1, Kirschke et al. 2013; Ciais et al. 2013).

7.4 Contemporary Global Methane Budget

Currently, source and sink processes of CH_4 are not accurately quantified despite several decades of research (Lassey and Ragnauth 2010), and there are still large uncertainties on estimated emissions and losses. The global sinks that remove tropospheric CH_4 has an uncertainty of about 20% (Ciais et al. 2013), anthropogenic sources have uncertainty range of ~30% (Kirschke et al. 2013; Ciais et al. 2013), while wetland emissions have uncertainty of 40% (Kirschke et al. 2013). The global atmospheric CH_4 budget is determined by many terrestrial and aquatic surface sources balanced primarily by one major sink in the atmosphere, and the atmospheric growth rate results from the balance between emissions and sinks (Kirschke et al. 2013).

Significant progress has been made using inverse modeling to quantitatively link regional sources and sinks, where inferred emissions are linked with photochemical sinks—tropospheric and stratospheric OH concentrations, and matched to atmospheric observations, and therefore, reducing the uncertainties (Bousquet et al. 2006). For example, using inversion techniques and dry air column averaged mole fractions of atmospheric CH_4 from the Thermal And Nuclear infrared Sensor for C Observations Fourier Transform Spectrometer (TANSO-FTS) on board Greenhouse Gases Observing Satellite (GOSAT), two-year average emissions based on monthly average CH_4 emission from January 2010 to December 2011 estimated at 537.3–540.4 Tg CH_4 yr^{-1} (Alexe et al. 2015). Inversion techniques have also showed that global CH_4 emissions have increased significantly since 2006, with much higher emissions during 2007–2010 period compared to the average emissions during 2003–2005 period (Bergamaschi et al. 2013). Inversion techniques allowed for the attribution of the observed increases spatially, to tropics and mid-latitudes of the Northern Hemisphere, and largely to anthropogenic sources (Bergamaschi et al. 2013). In addition, significant interannual variations in CH_4 emissions from wetlands and biomass burning were also identified that were superimposed on increasing trends of anthropogenic CH_4 emissions (Bergamaschi et al. 2013). Inversion of atmospheric measurements of CH_4 from surface stations estimated that global CH_4 emissions for the 2000–2009 period range from 526 to 569 Tg CH_4 yr^{-1} (Table 1). The total atmospheric oxidation range from 514 to 560 Tg CH_4 yr^{-1}, indicating a small imbalance of about 3 Tg CH_4 yr^{-1}, which is in line with the small atmospheric growth rate of 6 Tg CH_4 yr^{-1} observed between 2000 and 2009. The bottom-up models and inventories showed a larger global CH_4 emissions, ranging from 542 to 852 Tg CH_4 yr^{-1} (mean 678 Tg CH_4 yr^{-1}, Table 1). Reasons for the discrepancies between top-down inversion and bottom up inventories are still debated. Thus, upward re-evaluation of geological (Etiope et al. 2008) and freshwater (Walter et al. 2007; Bastviken et al. 2011 emission sources could account for the observed discrepancy. An ensemble of Atmospheric Chemistry models estimated an averaged total loss ranging from 592 to 785 Tg CH_4 yr^{-1} (mean 632 Tg CH_4 yr^{-1} during 2000–2009 decade (Lamarque et al. 2013), suggesting an imbalance of about 45 Tg CH_4 yr^{-1}. The observed average atmospheric growth rate during this period is estimated at 6 Tg CH_4 yr^{-1} (Dlugokencky et al. 2011). Unlike top-down inversions which have constrained OH fields, no constraint applicable to the sum of emissions in the bottom-up approach. Although top-down inversions can help in constraining global CH_4 emissions in the global CH_4 budget, they do not provide detailed resolution of mix of sources that is achieved by the bottom-up approaches, and thus provide limited information about emission and sink processes.

Based on the pre-industrial atmospheric CH_4 concentration of 722 ppb, the atmospheric CH_4 burden was 2042 Tg CH_4 (Dlugokencky et al. 2005) compared to the current atmospheric burden estimated at 4800 Tg (Table 2, Voulgarakis et al. 2013).

7.5 Atmospheric Chemistry of Methane

In addition to its effects on radiation energy balance and Earths' climate, CH_4 plays important chemical roles in the atmosphere, and its destruction with the OH radical in atmosphere initiates a chain of reactions that can affect tropospheric air quality and ozone formation. Therefore, changes in atmospheric CH_4 abundance are of substantial importance to atmospheric photochemistry. The chemical reactions that destructively oxidize atmospheric CH_4 affect the chemical state of the atmosphere through the products of reactions and through consumption of reactant species. The oxidation of CH_4 produces CO, CO_2, H_2O, H_2, and CH_2O, and also consume OH. The reaction pathways for CH_4 destructive oxidation affect tropospheric ozone (O_3) amounts, and they produce important quantities of stratospheric H_2O. Therefore, changes in atmospheric CH_4 concentration have caused changes in concentrations of O_3 and OH radical. In addition, stratospheric CH_4 reacts with chlorine atoms to form HCl, a reservoir species for chlorine atoms. Similarly, a portion of the flux of hydrogen atoms carried upward into the stratosphere in CH_4 escapes into space which represents a source of atmospheric O_2.

The OH is produced by the action of ultraviolet radiation (λ = 315 nm) on O_3 and water vapor (Eq. 7.1):

$$O_3 + hv \rightarrow O(^1D) + O_2 \tag{7.1}$$

The electronically excited O_2 atoms ($O(^1D)$) produced quenched in collision with N_2 and O_2 (Eq. 7.2) and then ozone is reformed (Eq. 7.3):

$$O(^1D) + N_2 \rightarrow O + N_2 \tag{7.2}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{7.3}$$

where, M = N_2, O_2, or any molecule which collides to stabilize O_3. Some $O(^1D)$ about 1% react with water vapor to produce hydroxyl radical (OH) (Eq. 7.4).

$$O(^1D) + H_2O \rightarrow 2OH \tag{7.4}$$

Net reaction:

$$O_3 + H_2O \rightarrow 2OH + O_2 \tag{7.5}$$

The OH is responsible for the removal of almost all trace gases from the atmosphere. Despite the fact that the global average mixing ratio of OH in the atmosphere is 4×10^{-14}, it is this ultra-minor constituent which is responsible for the first step in the removal of most natural and anthropogenic gases from the atmosphere (Crutzen 1995). The first oxidation step which utilizes OH and rapidly following reactions lead to compounds which are readily removed from the atmosphere by precipitation or uptake at the Earth's surface.

About 90% of atmospheric O_3 is present in the stratosphere, and only about 10% of the atmospheric O_3 is located in the troposphere, with volume mixing ratio in unpolluted environment ranging from 15 ppbv at low altitudes in Southern Hemisphere to about 100 ppbv in the upper troposphere. But this relatively small amount of O_3 in the troposphere governs the oxidation processes in the Earth's atmosphere through the formation of OH, and is responsible for absorption of solar ultraviolet (UV) radiation of wavelengths shorter than 310 nm. It leads to production of electronically excited $O(^1D)$ atoms which have enough energy to react with water vapor to produce OH (Eqs. 7.1–7.5). OH controls the atmospheric lifetime of many gases. The production of $O(^1D)$ is temperature and solar energy dependent. Thus, high levels of O_3 shortwave radiation and humidity favor production of OH. Abundance of water vapor is largely determined by the temperature. Thus, the primary formation of OH is controlled by solar ultraviolet radiation flux, dependent on overhead O_3 column as well as the local O_3 and water vapor concentrations (Lelieveld et al. 2004).

The OH has a short lifetime on the order of few seconds (Lelieveld et al. 2004), and its quantification is particularly challenging. Modeling becomes an essential tool to probe its spatial and temporal variability. About 40% of OH radicals react with CH_4 and its oxidation products, while 60% of OH react with CO. Therefore, oxidation of CH_4 has significant influence on tropospheric and stratospheric chemistry. The oxidation of CH_4 strongly affects the atmospheric budgets of OH and O_3 (Crutzen 1973). Chemistry—transport model studies have predicted OH decreases and atmospheric increases in CH_4 due to increases in CH_4 and CO emissions both of which consume OH. For example a 6% increase in CH_4 atmospheric lifetime from 1992 to 2050 (Lelieveld et al. 1998) and 13% increase in CH_4 lifetime in 2100 (Wild and Palmer 2008). The mechanism of CH_4 oxidation and the products that are formed are dependent on the concentration of nitrogen oxides (NO_x). In NO_x-poor environments, including marine areas, the free troposphere over the tropics, and most of the Southern Hemisphere, O_3 is destroyed and OH runs down (Crutzen 1979; Lelieveld et al. 2004). Therefore, in NO_x-depleted system, increase in CH_4 enhances OH loss, and atmospheric lifetimes of CH_4 increases. In NO_x-rich environments of Northern Hemisphere and planetary boundary layer of the tropics during dry season, where air is polluted or moderately dirty tropospheric air and all of the stratosphere, the oxidation of CH_4 by OH in the troposphere leads to the formation of formaldehyde (CH_2O), CO, and O_3 in the presence of sufficiently high levels NO_x (Wuebbles and Hayhoe 2002) and yield hydrogen oxides (HO and HO_2) (Cicerone and Oremland 1988; Crutzen and Zimmermann 1991). Therefore, in NO_x-rich environments, O_3 is formed, and OH radicals are recycled (Lelieveld et al. 2004). NO_x is an important component of local pollution in urban areas, and its increased presence results in O_3 formation (Eq. 7.1) that in turn increases OH production. Modeling has shown that increasing NO_x emission causes increase in global OH, and hence increased CH_4 sink (Fuglestvedt et al. 2000). Most current models suggest that an increase in CH_4 will decrease OH and increase O_3 throughout the troposphere (Wuebbles and Hayhoe 2002).

Destructive oxidation reactions with OH radical which removes CH_4 from the atmosphere are outlined in Eqs. 7.6–7.14:

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{7.6}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{7.7}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \tag{7.8}$$

$$CH_3O_2H + hv(\leq 330\ \mathrm{nm}) \rightarrow CH_2O + OH \tag{7.9}$$

$$\mathrm{Net:}\, CH_4 + O_2 \rightarrow CH_2O + H_2O \tag{7.10}$$

The CH_2O is an important intermediate in the removal processes of CH_4 and hydrocarbons as well as being important in general chemical reactivity of the atmosphere. Regardless of NO_x levels, CH_4 oxidation is responsible for the formation of much of CH_2O in the atmosphere. It is estimated that production of CH_2O in the atmosphere is in the order of 10^{14} g yr^{-1} (Lowe and Schmidt 1983; Wuebbles and Hayhoe 2002). Once generated, CH_2O is quickly destroyed by direct insolation. The photochemical breakdown of formaldehyde to CO occurs as follows:

$$CH_2O + hv(\leq 350\,\mathrm{nm}) \rightarrow H + CHO \tag{7.11}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{7.12}$$

$$CHO + O_2 \rightarrow CO + HO_2 \tag{7.13}$$

$$\mathrm{Net:}\, CH_2O + hv + 2O_2 \rightarrow CO + 2HO_2 \tag{7.14}$$

During the daytime, photolysis is the dominant loss process for CH_2O (Eqs. 7.11–7.14), while in the polluted atmospheres reactions with OH and hydroperoxyl are similar to photolysis degradation (Wuebbles and Hayhoe 2002) At night, CH_2O reacts with NO_3, however, it is a slow process compared to daytime (Wuebbles and Hayhoe 2002). The theoretical maximum yield of O_3 from CH_4 molecule oxidized all the way to CO_2 and H_2O is 5 O_3 molecules. Nevertheless, this maximum yield in never realized under actual atmospheric conditions because of competing reactions. When levels of NO_x are sufficiently high, peroxy radicals (HO_2, CH_3O_2) react exclusively with NO and all the CH_2O formed is photolyzed by the radical path (Eq. 7.14). The CH_2O and CO are important intermediates in the atmospheric process.

Based on the reaction sequences for CH_4, CH_2O, and CO in polluted and unpolluted environments, the effect of the complete oxidation of 1 mol of CH_4 results into increase of 0.4–0.5 and 3.6–3.8 mol OH and O_3, respectively in high NO_x (Crutzen 1973; Wuebbles and Hayhoe 2002), and decrease in OH ranging from −3.5 to −3.9 mol of OH in low NO_x environment (Wuebbles and Hayhoe 2002).

The destruction of OH depends on the OH concentration, methyl peroxide concentration, the methyl peroxide chemical reaction pathways and the heterogeneous removal rates of important intermediate species.

The alternative pathways are:

$$CH_2O + hv(\leq 350\,nm) \rightarrow CO + H_2 \tag{7.15}$$

$$CH_2O + OH \rightarrow CHO + H_2O \tag{7.16}$$

$$CHO + O_2 \rightarrow CO + HO_2 \tag{7.17}$$

$$\text{Net:}\, CH_2O + OH + O_2 \rightarrow CO + H_2O + HO_2 \tag{7.18}$$

The remaining CH_4 is destroyed by OH, Cl or $O(^1D)$ atoms in the stratosphere. A small fraction of CH_4 goes through the stratosphere to the mesosphere where a very short ultraviolet (UV) light, i.e., Lyman alpha radiation—121.6 nm) destroys CH_4 photolytically. The largest single sink of atmospheric CH_4 is its reaction with OH. It is estimated that 85–90% of CH_4 in the troposphere is destroyed by oxidation with OH. A complete oxidation of CH_4 yields CO_2 and H_2O:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{7.19}$$

The atmospheric lifetime of CH_4 ranges from 9 to 11 years with CO_2 and H_2O the eventual oxidation products (Prather et al. 2012; Holmes et al. 2013; Myhre et al. 2013). Although Eq. 7.19 is a simple and clear oxidation reaction, it does not describe the mechanism through which the atmosphere oxidizes CH_4. In the atmosphere, the process is initiated by OH radicals and not O_2 and it requires light. Altogether, the oxidation of CH_4, CH_2O and CO to CO_2 leads to loss of OH and HO_2 in NO_x-poor environments and a gain of O_3 in NO_x-rich environments. Generally, increases in NO_x emissions have been associated with more OH generation because NO_x generally leads to O_3 production which is the main source of OH, and NO_x-rich environments favor more secondary OH production through conversion of HO_2 to OH (Voulgarakis et al. 2013; Crutzen 1973).

In the troposphere, especially in the altitude range of 0–6 km, CH_4 oxidation consumes O_3, OH, and HO_2 in producing CO_2, H_2O, and H_2. The flow of CH_4 in the atmosphere and the products of its oxidation is illustrated in Fig. 7.7. Reaction with stratospheric OH is the dominant sink of CH_4, followed by that of Cl atoms. A fraction of H atoms that are released in CH_4 oxidation and from photochemical decomposition of H_2O in the stratosphere are subsequently released to space. The H atoms in the thermosphere and exosphere are furnished in large part by CH_4 oxidation. Therefore, temporal increase in CH_4 concentrations is also causing an increase in the rate of escape of H to space (Ehhalt 1986). Oxidation processes removes a range of environmentally important species from the atmosphere. Besides its role in CH_4 oxidation, OH is involved in removing other trace gases such as nitrogen oxides (NO_x), CO, non-CH_4 volatile organic compounds, and

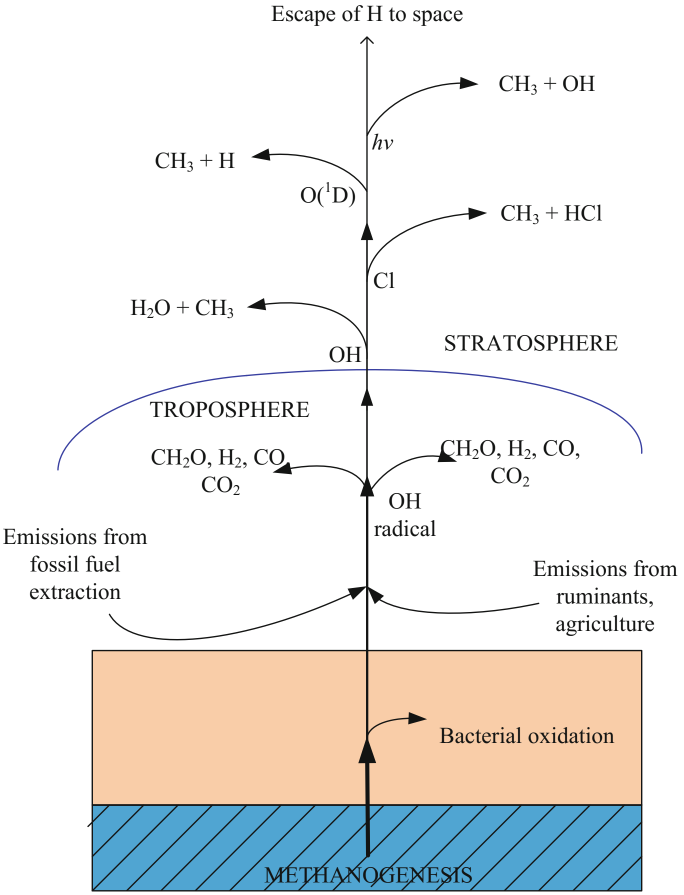

Fig. 7.7 Schematic illustration of the flow of CH_4 from several representative biological and abiogenic sources. The CH_4 oxidation occurs in sediments, waters, and the atmosphere. In the atmosphere, most methane is destroyed in the troposphere by OH radical, but 10–20% is transported upward to the stratosphere where the remainder is destroyed

ozone-depleting substances such as hydrofluorocarbons (HFCs) (DeMore 1996; Voulgarakis et al. 2013). Tropospheric oxidation depends heavily on the level of OH radical and its geographical distribution. A potentially important consequence of CH_4 oxidation is that of CH_4, CO, and OH perturbations. Reaction with OH is also the major sink of atmospheric CO, and the reactions of OH with CH_4 and CO suppress OH concentrations. The chemical coupling of CH_4 and OH leads to significant amplification of CH_4 emissions because increased CH_4 emissions decrease tropospheric OH which increases the CH_4 lifetime and thereby its concentration (Myhre et al. 2013; Holmes et al. 2013). Current increase in CH_4 is probably decreasing OH radical concentration, resulting into further increase in atmospheric CH_4 concentrations.

7.6 Biological Aspects of Methanogenesis

About 70% of the atmospheric CH_4 originates from biogenic sources (Conrad 2009), and biological processes under anoxic environment are the main biogenic source of atmospheric CH_4 emission. Commonly described methanogens microorganisms belong to domain archaea, kingdom Archaebacteria and phylum *Euryarchaeota* (Nazaries et al. 2013; Thauer et al. 2008) and share a set of bidirectional enzymes responsible for their respective metabolisms (Thauer 2011). However, archaea members of phylum Bathyarchaeota from coal beds with genetic potential to generate CH_4 been identified by DNA sequencing (Evans et al. 2015; Lloyd 2015). Coal bed methanogens have a potential to increase natural gas productivity from existing natural gas wells.

Anaerobic archaea are major contributors to global CH_4 cycling, and estimated to produce 1.0 Pg CH_4 yr^{-1}, with equal amount estimated to be oxidized archaeal methanotrophs (Reeburgh 2014). They produce CH_4 as the major product of their energy conserving metabolism in anaerobic respiration. All methanogens archaea characterized so far are strictly anaerobic respiration. They are a large and phylogenetically diverse group, which are classified into two classes: Methanobacteria and Methanococci, and six identified orders: *Methanobacteriales*, *Methanococcales*, *Methanomicrobiales*, *Methanosarcinales*, *Methanopyrales*, and Methanocellaces, which are further divided into 12 families (Liu and Whitman 2008; Offre et al. 2013; Nazaries et al. 2013). All of methanogenic archaea are obligate CH_4-producers that obtain all or most of their energy from methanogenesis. Methanogens are the only Archaea currently cultivated that are cosmopolitan, and are found in wide variety of the anaerobic environments on Earth. They are usually abundant where electron acceptors such as NO_3^-, Fe^+, and SO_4^{2-} are in short supply. In addition to temperate habitats, they are also common in environments of extreme temperatures, salinity, and pH. The common habitats of methanogens include marine and fresh water sediments, flooded soils, human and animal gastrointestinal tracts, termites, anaerobic digesters, landfills, geothermal systems, polar systems and heartwood of trees (Liu and Whitman 2008). Although obligate anaerobes, a recent study confirmed that methanogens are ubiquitous in aerobic soils and can actively produce CH_4 as soon as conditions changes to anoxic (Angel et al. 2012).

The methanogenesis pathway is a complex, and requires a number of unique co-enzymes and membrane-bound enzyme complexes for coupling to the proton motive force. The complexity and uniqueness of methanogenesis as a form of anaerobic respiration resides in requirement of six unusual co-enzymes—ferredoxin, methanofuran, tetrahydromethanopterin, coenzyme F_{420}, coenzyme M, and coenzyme B; a multistep pathway and several unique membrane-bound enzyme complexes coupled to the generation of a proton gradient driving ATP synthesis (Ferry 2010a; Nazaries et al. 2013). The three main methanogenic substrates are (i) CO_2, (ii) acetate, and (iii) methyl group containing compounds such as methanol, methylated amines, and methylated sulfides. Several methanogenic pathways that rely on these substrates have been described for CH_4 production: (i) hydrogentrophic and formatrophic methanogens, (ii) acetotrophic methanogens, and (iii) methylotrophic methanogens. In hydrogenotrophic and formatrophic methanogenesis, CO_2 is reduced with H_2 or formate as electron donors, to form CH_4 through formyl, methylene and methyl levels (i.e., methanol reduction with H_2). In acetotrophic methanogenesis, acetate is split into CH_4 and CO_2 after activation to acetyl-CoA and then split into methyl-CoM and CO (i.e., fermentation of acetate). In methylotrophic methanogen, methyl is reduced to CH_4 and CO is oxidized to CO_2 (i.e., dismutation of methylated compounds such as methanol, methylamines, dimethylsulfide (DMS) or methanethiol) (Liu and Whitman 2008; Ferry 2010b). In methyl containing compounds, *Methanosarcinales* and *Methanosphaera* convert methylated compounds by first transferring methyl group to protein (corrinoid) and then to coenzyme M. Methyl-CoM then enters the methanoganesis pathway and is reduced to CH_4 and CO_2 (Ferry 2010a).

Whereas most cultivated methanogens reduce CO_2 with H_2, only members of *Methanosarcinales* have the ability to produce CH_4 from the fermentation of acetate and dismutation of methylated compounds. The recently discovered methanogenic *Thermoplasmata* reduce methanol with H_2 (Dridi et al. 2012; Paul et al. 2012), and might also use methylamines as methanogenic substrate (Poulsen et al. 2013). Currently one of these methanogenic metabolisms have been found in bacteria or eukaryotes (Offre et al. 2013). Acetate is the major intermediate in anaerobic food chain, and about two-thirds of biologically generated CH_4 and released to the atmosphere by archeal methanogenesis is derived from acetate. However, only two genera—*Methanosacrcina* and *Methanosaeta* are known to use acetate (Jetten et al. 1992). The reduction of CO_2 accounts for the rest of the archeal contribution to atmospheric CH_4, with minor amounts of CH_4 produced by the dismutation of methyl compounds (Ferry 2010b).

Methanogenic archaea have also been found in oxic environments including various aerated soils (Angel et al. 2012) and the oxygenated water column of oligotrophic lake (Grossart et al. 2011). The methanogens in aerated soils become active under wet anoxic conditions (Angel et al. 2012) and those in oxygenated lake waters are attached to photoautotrophs, which might enable anaerobic growth by supply of methanogenic substrates (Grossart et al. 2011). Several other processes, such as the microbial decomposition of methylphosphonate could be responsible for CH_4 production in oxygenated waters (Keppler et al. 2009), and fungi (Lenhart et al. 2012) and plants (Bruhn et al. 2012) are possible sources of CH_4 in aerated soils. The global significance of these alternative aerobic methanogenic pathways remains to be assessed.

Methanogenic archaea engage in various syntropic partnerships with anaerobic bacteria, protozoa, and fungi (Stams and Plugge 2009) that involve the transfer of electrons from a fermentative organism to the methanogen through carrier molecule such as H_2 or acetate (Sieber et al. 2012). Syntrophy is a tightly coupled mutualistic interaction between H_2/formate-producing and H_2/formate using microorganisms where the pool size of intermediates that are exchanged between the partners must be kept very low for efficient cooperation among the microorganisms to occur.

It occurs throughout the microbial community. The methanogens use the carrier molecule as electron donor for energy conservation, and the fermentative organism gains energy from the redox reaction that produces the electron carrier only if the methanogens oxidize the carrier molecule, keeping the carrier at a low concentration. Syntropic interactions enable methanogenesis when methanogenic substrates are limiting, and their establishment can also lead to increased CH_4 production rates (Kato et al. 2012). The global biogeochemical impact of syntropic interaction involving methanogenic Euryarchaeota is considerable as they enable the complete degradation of complex organic molecules to CO_2 and CH_4 in methanogenic habitat (Sieber et al. 2012). Acetotrophic methanogens can also produce H_2 and support the H_2-dependent dechlorination of xenobiotic compounds by dehalorespiring microorganisms (Heimann et al. 2006), further broadening the biogeochemical significance of the interactions involving methanogenic archaea.

7.6.1 Methane Oxidation in Soils

The oxidation of CH_4 is carried out by bacteria and archaea. The bacterial methanotrophs are gram-negative bacteria and generally only grow on CH_4 or methanol as a source of C and energy. Methanotrophic bacteria are often found at the anoxic/oxic interphase of various habitats such as geothermal reservoirs, landfills, soils, peat bogs, wetlands or aquatic environments and sediments where they consume the CH_4 arising from methanogenesis and are able to lower the CH_4 emissions (Conrad 1996). These methanotrophs can oxidize high concentrations of CH_4 (>100 ppm) and are sometimes referred to as low affinity methanotrophs. Other methanotrophs have the ability to oxidize CH_4 at atmospheric concentrations (~ 1.8 ppm) and are referred to as high affinity methanotrophs (Bender and Conrad 1992). Methanogenic bacteria belong to kingdom *Eubacteria* and two phyla—*Proteobacteria* and *Verrucomcrobia*. A total of 21 genera and at least 56 species have been identified (Nazaries et al. 2013).

The atmospheric CH_4 sink occurs in upland forest soils, and this fraction is attributed to high-affinity methanotrophs (Kolb 2009). In temperate soils, moisture ranging from 60 to 100% water-filled pore space (WFPS), decreases the CH_4 oxidation rates. This is attributed to limited O_2 availability and soil gas diffusivity, particularly because CH_4 transport in water is 10,000 times slower than in air (Castro et al. 1995). In contrast, when moisture is low (<12% v/v), CH_4 consumption is also inhibited by desiccation and increased osmotic stress (Jäckel et al. 2001). The effects of temperature on CH_4 oxidation are inconsistent, suggesting that methanotrophic bacteria can adapt to different temperatures. Overall temperatures <10 and >40 °C seem to decrease methanotrophic activity significantly in forest and landfill cover soils possibly as a result of inhibition of mesophilic methanotrophic activity (Semrau et al. 2010). Methanotrophs are also adaptive to wide range of pH—from pH 3.5 to pH 8, probably due to existence of acido-, neutro- and alkaliphiles. Other soil characteristics such as bulk density, porosity, WFPS are closely linked to water content and therefore influence O_2, availability and diffusion of CH_4 in soils. In addition, soil texture is also a strong regulator of CH_4 flux (Castro et al. 1995).

Unlike methanotrophic bacteria, methanotrophic archaea are strict anaerobes that gain energy by coupling the oxidation of CH_4 to the reduction of SO_4^{-2} (Thauer 2011). Methanotrophic archaea belongs to Euryarchaeota and all are representatives of a single taxonomic class of Methanomicrobia along with various methanogenic archaea (Offre et al. 2013). They thrive in anoxic environment where both CH_4 and SO_4^{2-} are present, which occurs in marine sediments, where their habitat is restricted to the SO_4^{2-}—CH_4 transition zone. CH_4 oxidizing archaea have also been detected in anoxic water columns, hydrothermal vents, soils, aquifers, and freshwater habitats. Their physiological settings differ widely which indicates that archaeal methanotrophs are physiologically diverse.

7.6.2 Methane Oxidation in Marine Environments

Anaerobic oxidation of CH_4 exerts strong control over ocean CH_4 emissions, which accounts for only 2% of the CH_4 released to the atmosphere. The process consumes an estimated 20–300 Tg CH_4 yr^{-1}, which is equivalent to 5–60% of the global annual CH_4 flux to the atmosphere (Smemo and Yavitt 2011). Global estimates of anaerobic oxidation of CH_4 in oceanic environments suggest that large fraction (>50%) of gross annual production in marine systems is consumed by anaerobic methanotrophs before CH_4 is even released to the ocean waters and about 90% of CH_4 produced in marine sediments is oxidized by microorganisms before it reaches the surface (Reeburgh 2007). Many aspects of the physiological mechanisms of anaerobic oxidation of CH_4 under marine environments remains mysterious and difficult to interpret, however.

The anaerobic CH_4 oxidation in the ocean has been mostly attributed to the CH_4-oxidizing activity of anaerobic methanotrophic archaea, but other microorganisms may also be involved (Beal et al. 2009), their identity and contribution to the global CH_4 has not been determined. The ability of anaerobic methanotrophs to respond to potential increase in oceanic CH_4 production, which could result from an accelerated melting of the large reservoir of CH_4 hydrates present in the seabed (Boswell and Collett 2011) is uncertain however. Coastal regions comprise small area of the Earth's surface, but coastal wetlands are estimated to emit 40–60 Tg CH_4 yr^{-1} to the atmosphere, accounting for 7–30% of the global annual fluxes of CH_4 (Dentener et al. 2003). Coastal wetlands regions also play significant role in cycling CH_4, however, few direct measurements of CH_4 consumption are available (Van der Nat et al. 1997; King et al. 1990), and particularly anaerobic oxidation of methane in coastal habitats is unknown. The projected rise in sea level may cause a dramatic shifts in biogeochemical functioning of coastal sediments through changes in salinity and availability of electron acceptors including sulfate and iron and cause increase in CH_4 fluxes from these regions (Weston et al. 2011).

7.6.3 Methane Oxidation in the Atmosphere

In addition, oxidation of CH_4 occurs in the atmosphere worldwide, but the sources of CH_4 are not uniformly distributed. For example, over the most recent 1000 years, it has been shown that the Greenland CH_4 exceeded that of Antarctica by 24–58 ± 10 ppbv (Etheridge et al. 1998), and over 10,000 years the difference between Greenland CH_4 concentrations and Antarctica has been estimated at 33 ± 7 ppbv. Therefore, varieties of processes at regional and global complexities of both C cycle and climate system may have contributed to the trends observed in ice core record of Holocene CO_2 and CH_4.

The CH_4 measurements from the Law Dome site in Antarctica show small variations that parallel the CO_2 trends over the most recent millennium including a decrease of 40 ppbv coinciding with the CO_2 decrease in 16th and 17th centuries (Etheridge et al. 1998). Correlations between decrease in CH_4 and lower temperatures reconstructed during 15th and 16th centuries suggests that climate change may have reduced CH_4 emissions by wetlands during this period. The maximum natural rates of change in atmospheric CO_2 and CH_4 during the most recent millennium were at least an order of magnitude smaller than current anthropogenic rates of change, and the natural variations were much less persistent than the increasing trends of the most recent two centuries.

Extrapolated trends in CH_4 measurements at these sites and at the Dryas 3 site in Greenland are likewise consistent with recent atmospheric measurements (Stauffer et al. 1985; Etheridge et al. 1992). Similarly, atmospheric CH_4 concentration decreased from early Holocene to about 5000 years and then increased gradually by about 100 ppbv between 5000 and 1750 (Fig. 7.3). Both Greenland and Antarctica ice cores indicate that atmospheric CH_4 concentrations varied much wider during Holocene Epoch, with its concentrations decreasing from near 700 ppbv at 10,000 years to concentrations >600 ppbv at 5000 years, followed by gradual return to near the 700 ppbv by 1000 years BP (Flückiger et al. 2002; Chappellaz et al. 1997; Blunier et al. 1995). Alternative hypothesis attributes atmospheric CH_4 increase between 8000 and 1000 years to expansion of boreal wetland source areas (Blunier et al. 1995; Chappellaz et al. 1997; Velichko et al. 1998). Others have attributed late Holocene atmospheric CH_4 increase partly to onset of early human cultivation of rice (Ruddiman 2007; Subak 1994; Chappellaz et al. 1997) and widespread domestication of ruminants after 5000 years (Ruddiman 2007; Fuller et al. 2011). A study by Kaplan et al. (2006) suggested that part of the late Holocene CH_4 increase could be explained by anthropogenic sources.

7.7 Methane Clathrate Hydrates

Gas hydrates are ice-like crystalline solids that form from mixtures of water and light natural gases such as CH_4, CO_2, ethane and butane. The CH_4 hydrates are nonstoichiometric solid structures composed of cages of water molecules surrounding CH_4 molecules in high pressure and low temperature conditions stabilized by van der Waal type interactions (Hester and Brewer 2009; Xu and Li 2015). The water molecules are arranged in a rigid framework of cages called clathrates, many of which are occupied and stabilized by a molecule of CH_4. The occurrence of CH_4 hydrates is controlled by an interaction of temperature, pressure, gas saturation, and water; and local chemical conditions combine these factors to make them stable (Kvenvolden 1993b; Demirbas 2010a). Most marine gas hydrate that have been analyzed are CH_4 hydrates. Such conditions can exist in ocean bottom sediments at water depths below 500 m (Kvenvolden 1993a) or in the Arctic, where hydrate forms beneath the permafrost (Demirbas 2010a). Hydrates occur in these two type of settings because the temperature-pressure conditions in these settings are within the hydrate stability field (Lerche and Bagirov 1998). Gas hydrates occur in pore spaces of sediments, and form cements, nodules, veins, or layers. Given a favorable combination of pressure and temperature, and availability of free CH_4 and water, gas hydrates can form and remain stable (Kvenvolden 1993b). The hydrate deposits themselves may be several hundred meters thick (Demirbas 2010a). In the oceans, gas hydrate is generally found at depths between 300 and 4000 m and at temperatures between 2.5 and 25 °C (Max and Dillon 1998). The existence of CH_4-rich natural hydrate in large quantities was recognized in 1960s (Makogon 1965), and currently over 90 sites have been directly or indirectly identified to contain natural gas hydrates.

The term CH_4 hydrate and gas hydrate are often used interchangeably and refers to these CH_4-water crystalline structure called clathrate. Clathrates are crystalline solids which look like ice and occur when water molecules form a cage-like structure around smaller guest molecules. The most common guest molecules are CH_4, ethane, propane, isobutene normal butane, N_2, CO_2 and H_2S, of which CH_4 occurs most abundantly in natural hydrates (Mahajan et al. 2007). Clathrates are stable under specific pressure-temperature conditions. Under appropriate pressure, they can exist at temperatures significantly above the freezing point of water. The maximum temperature at which a clathrate can exist depends on pressure and the gas composition. For example, CH_4 and water at 41 atmosphere pressure forms a hydrate at 278 K, whereas, the same pressure with 1% propane forms hydrate at 281 K (Demirbas 2010b). Hydrate stability can also be influenced by other factors such as salinity (Archer 2007). Hydrate formation is bound by temperature and pressure. Hydrate contains large amount of gas. For example, 1 m^3 of hydrate disassociates at atmospheric temperature and pressure to form 164 m^3 of CH_4 and 0.8 m^3 of water (Kvenvolden 1993b). With pressurization, hydrates remain stable at temperatures up to 291 K. Because of the requirements of pressure and temperature, and also the requirement of relatively large amounts of OM for bacterial methanogenesis, clathrates are mainly restricted to two regions: (i) high latitudes, and (ii) along continental margins in the oceans (Kvenvolden 1993a, 1998).

Estimates of the size of the CH_4 reservoir sequestered as hydrates are enormous. Because these CH_4 hydrates are frequently close to the sediment–water interface and because they represent such a large reservoir, hydrate stability has been a major concern. There is extensive evidence of slides and craters on ocean shelves, presumably caused by destabilization and release of gas-phase CH_4 (Hovland and Judd 1988), but little information on the magnitudes of CH_4 release needed to form these features exist. While CH_4 is an important part of the natural C cycle, little is known about the role of CH_4 hydrates in the global budget (Cicerone and Oremland 1988). Specifically, much remains unknown about the processes leading to CH_4 generation, its transport, and transformations within sediments and its significance in global C budgets (Hovland and Judd 1988; Dickens 2003a; Torres et al. 2004). The CH_4 hydrates have a latent heat of fusion quite similar to that of water (Sloan 1998). Therefore, the decomposition of hydrates is a matter of heat flux and not a rise in temperature. Hydrate stability is not a matter of pressure–temperature conditions alone, as CH_4 concentrations substantially higher than saturation values are required for hydrate formation and stability (Sloan 1998).

7.7.1 Origin and Formation of Methane Hydrates

The CH_4 in gas hydrates is dominantly generated by bacterial anaerobic degradation of OM in low O_2 environments. In ocean, CH_4 could be produced by bacteria near the sea floor that are decomposing organic sediments or originate from oil deposits leak in the sea floor bottom through faults and cracks. Bacterial CH_4 formed in early diagenesis of OM and thermogenic gas leaking to the surface from a deep thermogenic gas accumulation can form a gas hydrate in the same continental shelf sediment. There are hydrates forms in both primary and secondary pore spaces and fractures in sediments as a diagenetic mineral (Sloan 1998). Sub-seabed CH_4 within the continental margin sediment is produced primarily by microbial or thermogenic processes. In the thermogienic process, thermal cracking of organically derived materials forms petroleum hydrocarbons, including CH_4, generally at a considerable depths (>2 km) in sedimentary basins where temperatures exceed 273 K, or thermal degradation of oil at even greater depths, and also by maturation of coal (Desa 2001). However, it is unknown how CH_4 is trapped in conditions favorable for CH_4 retention within the lattice.

7.7.2 Methane Hydrate Reservoir

CH_4 is an important component of the global C cycle, however, much remains unknown about the processes leading to CH_4 generation, transport, and transformation within the sediments, and its significance in global C budgets (Hovland and Judd 1988; Dickens 2003b; Torres et al. 2004). CH_4 comprises more than 99% of the hydrocarbon gases in most natural gas hydrate. Minor quantities of CO_2 and H_2S are often present, but because the main component is CH_4 the gas hydrate is called CH_4 hydrate (Sloan 1998; Kvenvolden and Lorenson 2001). The CH_4 hydrate recovered from the Gulf of Mexico show that CH_4 hydrates are often accompanied by significant amounts of ethane and propane and higher molecular weight hydrocarbon gases (Sloan 1998; Sassen and Macdonald 1994). The information on molecular composition of hydrocarbon gases in gas hydrate samples, coupled with isotopic composition ($\delta^{13}C$ and deuterium) of CH_4 provide basis for interpreting the origin of gas. In most of CH_4 hydrate samples CH_4 has C isotopic composition lighter than −60‰, suggesting that the CH_4 is mainly microbial in origin. Microbial CH_4 in CH_4 hydrate may have either been generated in place from methanogenic processes taking place in shallow sediment, migrated short distances, or recycled during processes of hydrate formation and dissociation accompanying sedimentation (Paull et al. 1994). In contrast, CH_4 with C isotopic compositions heavier than −60‰, accompanied by significant amounts of higher molecular weight hydrocarbons, such as ethane, propane and larger hydrocarbon gases is of thermal origin. Most natural gas hydrate contains CH_4 that was generated by microbial processes. The CH_4 with thermal origin occurs in gas hydrates only where deeper deposits of thermogenic natural gas provide a source of CH_4 (Kvenvolden and Lorenson 2001). The estimates of CH_4 content of CH_4 hydrate are highly speculative, but they suggest that CH_4 quantities are very large (Kvenvolden 1999). The potential size of the ocean CH_4 hydrate reservoir estimated based on two models for CH_4 hydrate formation: (i) in situ bacterial production, and (ii) a fluid expulsion model suggested CH_4 hydrate reservoirs of 14,000 and 75,000 Pg C, respectively (Gornitz and Fung 1994). A consensus value of 10,000 Pg C for the amount of CH_4 hydrate has been suggested (Kvenvolden 1993a, b; Kvenvolden and Lorenson 2001; Archer et al. 2009; Burwicz et al. 2011). This is a large quantity, nearly 2000-fold larger than the atmospheric CH_4 inventory and ~30% of the ocean dissolved inorganic carbon reservoir. It is estimated as one of the largest C reservoir on Earth (Milkov 2004; Reeburgh 2007), containing about ten times more than the atmosphere. The need for energy is driving much of the current natural hydrate research and clathrate exploration programs (Collett 2002; Demirbas 2010b). Conversely, the vast quantities of hydrates in marine sediments pose a risk as geo-hazard, which have been implicated in past climate change event (Kennett 2003). This section focuses on its role on global C cycle and the possible impact on the global climate change. When warmed or depressurized, CH_4 dissociates into water and CH_4. Discharge of large amount of CH_4 into the atmosphere causes global warming. Direct transfer of even a small fraction of the ocean hydrate CH_4 to the atmosphere would have a catastrophic effects on climate, a process proposed as both an initial driver of positive feedback to climate change (Dickens et al. 1995; Archer 2007).

7.7.3 Methane Hydrate Decomposition Climate Change

The possible connection between climate and hydrates have been of interest to geoscientists. Natural hydrates may affect climate because when they are warmed or depressurized they decompose and dissociate into water and CH_4. Discharge of large quantities of CH_4 into the atmosphere will cause global warming. The rapid climate change in the past from cold glacial period to warmer interglacial periods has been indeed attributed to large release of CH_4 from gas hydrates. Some models have linked these observations with climate change caused by hydrates dissociation and vice versa (Blunier 2000; Kennett et al. 2000). It is suggested that glaciation and/or sea level fall will reduce hydrostatic pressure on sediments of shelf and slope at mid-latitudes, thereby destabilizing hydrates and consequently releasing CH_4 into the atmosphere. The CH_4 released will cause rapid warming, which will lead to dissociation of hydrates in the permafrost regions and shallow continental margins of high latitude regions, a positive feedback causing further warming. As a result, ice in the higher latitudes will melt and increase sea level. The rise in sea level will increase the hydrostatic pressure and the sediments shelf and slope at mid-latitudes initiating negative feedback that inhibit further release of CH_4 from hydrates. The geologic evidence, primarily from the C isotopic record of deep-sea cores, for CH_4 releases in the past exist (Dickens et al. 1995; Katz et al. 1999).

The CH_4 hydrates are located in shallow submarine geosphere, which is a finely balanced system in equilibrium with all its components, including sediment, pore water, fluid flows, pressure, temperature, overlying water, and hydrate. Removal of any one component of this equilibrium may destabilize the whole system leading to irreversible damage. The CH_4 Hydrates may be in steady state, but they cannot be stable because of differences in the chemical potential of CH_4 in the hydrate phase and the adjacent dissolved interstitial CH_4 (Dickens 2003a). Thus, CH_4 hydrates must be viewed as dynamic, with large and unknown fluxes to and from the ocean. The mechanisms involved in destabilizing CH_4 hydrate include deep-water warming (Hesselbo et al. 2000; Norris and Rohl 1999) and mass wasting of continental slopes (Vogt and Jung 2002). The destabilizing factors may either be natural, anthropogenic or combination of both. The CH_4 hydrates are susceptible to the influence of temperature (Glasby 2003). Due to enormous amount of CH_4 stored in CH_4 hydrates worldwide, their destabilization have the potential to affect global climate and geological environment at a catastrophic scale.

The rate and pathway by which CH_4 gas is released from hydrate on sea floor and may be transferred to the atmosphere is still a matter of debate. An understanding of the rate of contemporary hydrate-derived CH_4 additions to the ocean is essential to evaluating the role of hydrates in the global CH_4 budget. However, accurate measurements which could permit this estimate to be made is challenging because: (i) no means of discriminating between hydrate CH_4 and diagenetically produced CH_4, (ii) CH_4 released by dissociating hydrates is effectively oxidized by microbially mediated processes in anoxic sediments (Reeburgh 1980; Alperin and Reeburgh 1984), as well as in the adjacent oxic water column (Valentine et al. 2001), therefore, elevated CH_4 concentrations or "hot spots" are rarely observed, and (iii) hydrates collected by coring or dredging decompose rapidly, and laboratory studies are difficult if not impossible to conduct at sea.

7.7.4 How Can We Estimate the Rate of Methane Clathrate Decomposition?

Methane clathrate decomposition has been implicated in the Latest Paleocene Thermal Maximum (~55 Ma) by an extraordinary injection of isotopically light carbon into the carbon cycle (Dickens 2000, 2001) and in Quaternary interstadials as indicated by observations of isotopically light foraminifera in Santa Barbara Basin sediments (Kennett et al. 2000). Research on CH_4 clathrates has been advanced by using remotely operated vehicles (ROVs), which can be equipped not only to synthesize hydrates in situ under appropriate pressure–temperature conditions (Brewer et al. 1997, 1998), but to locate seeps for sampling and to place acoustic beacons for longer-term stability experiments as well. Direct measurements of the decomposition rates of pure CH_4 and CO_2 hydrates in a seafloor setting nominally within the gas hydrate pressure-temperature stability zone have been made recently (Rehder et al. 2004). Their rates represent end members because of the flow field and undersaturation. The water-column CH_4 oxidation rate measurements of (Valentine et al. 2001) were conducted adjacent to seeps in the Eel River Basin that were previously located with an ROV. These oxidation rate measurements were conducted with tracer additions of 3 H–CH_4, and showed the highest rates near the bottom. These instantaneous rate measurements are difficult to interpret in a dynamic advecting coastal environment, but the fractional turnover rates can be used to infer a CH_4 turnover time of ~1.5 years in the deep waters. The depth-integrated rates (5.2 mmol CH_4 m^{-2} yr^{-1}) can be used to estimate total oxidation for the 25 km^2 vent field. The amount of CH_4 emitted is unknown, so it is not possible to estimate the oxidized fraction, but results from a closed system oxidation model applied to $d^{13}CH_4$ measurements suggested that ~45% of the added CH_4 was oxidized. Grant and Whiticar (2002) concluded from observations of isotopically heavy $d^{13}CH_4$ at Hydrate Ridge that substantial aerobic CH_4 oxidation occurred there. These isotopic enrichment measurements indicate cumulative CH_4 oxidation, but provide no rate information. Clearly, many more direct CH_4 oxidation rate measurements similar to those of (Valentine et al. 2001) are needed.

Recent work indicates that it may be possible to discriminate between hydrate–CH_4 and diagenetic–CH_4 with measurements of $^{14}CH_4$. If hydrates are formed by fluid expulsion, they will probably involve CH_4 from deep sources and will probably contain no radiocarbon; if they are formed by in situ bacterial production, the radiocarbon age will depend on the age of the substrate Winckler et al. 2002) reported radiocarbon measurements on CH_4 from massive CH_4 hydrates collected at Hydrate Ridge, Cascadia margin, and showed that they, as well as the unpublished results, are devoid of radiocarbon, indicating that there are no recent (^{14}C-active) contributions to the hydrate reservoir. Measurements of noble gases in hydrates (Winckler et al. 2002) showed that light noble gases are not incorporated into the hydrate structure, but that significant quantities of the heavier noble gases—argon, krypton, and xenon—are present. The heavy noble gases are potential secondary tracers of hydrate decomposition.

7.8 Conclusions

The atmospheric concentration of CH_4 has increased dramatically over the last century and continues to increase. The atmospheric concentration increase is a result of change in both global natural and anthropogenic emission sources. Emission of CH_4 is mainly the result of environmental processes such as methanogenesis in wetlands and other anoxic environments such as rice fields, rumen of ruminant animals and landfills. Additional sources include geological sources such as fossil fuel production and CH_4 hydrates. The global CH_4 emissions based on inversion of atmospheric measurement of CH_4 from surface stations for 2000–2009 are 553 ± 27 Tg CH_4 yr^{-1}. The total loss of atmospheric CH_4 is 550 ± 36 Tg yr^{-1} indicating imbalance of 3 Tg CH_4 yr^{-1}, the global total emissions based on bottom-up models and inventories is 678 ± 136 Tg CH_4 yr^{-1}. The total loss is 632 ± 40 Tg CH_4 yr^{-1}, with an imbalance of about 45 Tg CH_4 yr^{-1} compared to annual atmospheric growth rate of 6 Tg CH_4 yr^{-1}, indicating that bottom-up models may overestimate the global CH_4 budget. The top-down inversion have constrained OH fields, but there is no constraint applicable for sum of emissions in the bottom-up approach. Budget analysis have confirmed the causal role of human activities in this increase, however, significant uncertainties remain in understanding the factors that affect emissions from diverse sources and how these will change over time as a result of global climate change. Uncertainties in how the sources and sinks of CH_4 will change in future limit the ability to develop meaningful climate change policies aimed at controlling CH_4 emissions. The renewed increase in 2007 after a period of stabilization between 1999 and 2006 has created a renewed the debate about the future levels of CH_4. The increase is consistent with higher emissions from wetlands and fossil fuel burning, although the relative contributions remains uncertain. This increase is considered the first sign of the important biogenic positive feedback to climate change—the response of the wetlands to increases in global temperatures projected to occur in this century. Given the potential importance of CH_4 emissions as a positive feedback to anthropogenic climate change and other perturbations, it is of paramount importance that research addresses the knowledge gaps in CH_4 sources, sinks, and biogeochemical processes responsible for changes in emission. More research is needed to fully understand the CH_4 growth rate and its future trajectory. Complete analysis requires increased coordination between programs measuring atmospheric abundances, isotopic ratios, and modeling effort that couple biosphere and ocean biogeochemistry with atmospheric processes.

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Chapter 8
Mitigation of Climate Change: Introduction

Abstract The annual global greenhouse gas (GHGs) emissions have continued to grow since the industrial revolution. The dominant driving force for the anthropogenic GHGs emission include population growth, economic growth, fossil fuel consumption and land use change. Since the beginning of industrial revolution to 2015, cumulative anthropogenic carbon dioxide (CO_2) emission of 600 ± 70 Pg C were released to the atmosphere, causing an increase in atmospheric CO_2 relative abundance of 144% compared to pre-industrial era. The atmospheric concentrations of methane (CH_4) and nitrous oxide (N_2O) have also increased significantly. As a result, changes in climate has caused impacts on natural and human systems across the globe, and continued GHGs emission will cause further climate change impacts. Accurate assessment of anthropogenic CO_2 emissions and their redistribution among the atmosphere, ocean and terrestrial biosphere provides better understanding of C cycling and also support the development of climate policies, and project future climate change. The mitigation options available combine measures to reduce energy use and CO_2 intensity of the end use sectors, reduction of net GHG emissions, decarbonization of the energy supply, and capture and sequestration of C through enhancement of natural C sinks or by engineering techniques. There has also been emphasis on engineering of climate as an alternative mitigation option. Geoengineering, a global large-scale manipulation of the environment, is considered as one of the effective means of mitigating global warming caused by anthropogenic greenhouse gases (GHGs) emission. Assessment of technical and theoretical aspects of solar radiation management (SRM) and carbon dioxide (CO_2) removal methods (CRM) as well as their potential impacts on global climate and ecosystems will be reviewed. Most of the proposed geological engineering methods involving land or ocean will use physical, chemical, or biological approaches to remove atmospheric CO_2, while those proposed for atmosphere or space will target radiation without affecting atmospheric CO_2 concentration. The CRM schemes tend to be slower, and able to sequester an amount of atmospheric CO_2 that is small compared to cumulative anthropogenic CO_2 emissions. In contrast, SRM approaches have relatively short lead times and can act rapidly to reduce temperature anomaly caused by GHGs emission. Overall, current research on geoengineering is

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scanty and various international treaties may limit some geoengineering experiments in the real world due to concerns of an unintended consequences.

Keywords Decarbonization of energy supply · Carbon capture · Geoengineering · Kaya identity · Climate engineering · Carbon sequestration in the ocean

Contents

8.1 Introduction

The concentration of greenhouse gases (GHGs) including carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) in the atmosphere has been steadily increasing since the beginning of the Industrial Revolution in 1750. The CO_2 is the largest component of anthropogenic GHG, while CH_4 is the second most important GHG emitted by human activities. Anthropogenic CO_2 emissions from the combustion of fossil fuels have been the main contributor to the increasing CO_2 concentration in the atmosphere, followed by CO_2 emissions from land use and land use change (LULUC). Cumulative anthropogenic CO_2 emissions of 600 ± 70 Pg C (2200 ± 257 Pg CO_2) were released to the atmosphere between 1750 and 2015, of which, 260 ± 5 Pg C or about 40% of these anthropogenic CO_2 emissions (953 ± 18 Pg CO_2) have remained in the atmosphere since 1750, causing 144% increase in atmospheric CO_2 relative abundance from 1750 to 2015 (WMO 2016). The rest was removed from the atmosphere by sinks and stored in the natural carbon (C) cycle reservoir (Le Quéré et al. 2015, 2016). The natural sinks—ocean and terrestrial uptake accounts approximately equal measure, with ocean absorbing about 30% of the emitted anthropogenic CO_2 and causing ocean acidification. Terrestrial uptake consists of vegetation and soil sinks. The relative abundance of the atmospheric CH_4 and N_2O has also increased by 254% and 121, respectively relative to 1750 concentrations (WMO 2016). Anthropogenic CH_4 emissions are due to a wide range of activities, including production and transport of fossil fuels, livestock, rice cultivation, and decomposition of organic waste in solid waste landfills. The N_2O is emitted during agricultural and industrial activities and also during combustion of biomass.

Over the past 10,000 years during Holocene, the planet enjoyed a favorable stable climate window until humans flourished as a dominant force for change after industrial era, rapidly expanding their influence and exceeding a global geological change force. Humans have become a major transforming force that is rapidly pushing the planet towards new, undesirable state as the consensus continues to emerge about a future, hotter planet that will make it difficult with a sustainable society (Lenton et al. 2008). Energy is critical to global prosperity, as it underpins economic growth, social development, and poverty reduction. It has fueled global economic development since the Industrial revolution, and as many countries continue to aspire a more inclusive economic development, energy supply will continue to remain the major solution. Fossil fuels provide more than 80% of global energy needs, and the growing energy demands has led to increasing GHG emissions. Fossil CO_2 emissions have grown substantially over the past two centuries (Fig. 8.1). The energy sector generates approximately two thirds of global GHG emissions and more than 80% of total CO_2 emissions (Fig. 8.2). In 2012, energy sector produced 8.7 Pg C, the largest share of which came from power generation (IEA 2014). The CO_2 emissions are set to continue to grow, mainly driven by increases in emission from developing countries. Since economic growth and social development are coupled with increasing GHGs emission, the challenge of the 21st century is to decouple the two so as to achieve economic growth and social development while also achieving significant reductions in GHG emissions.

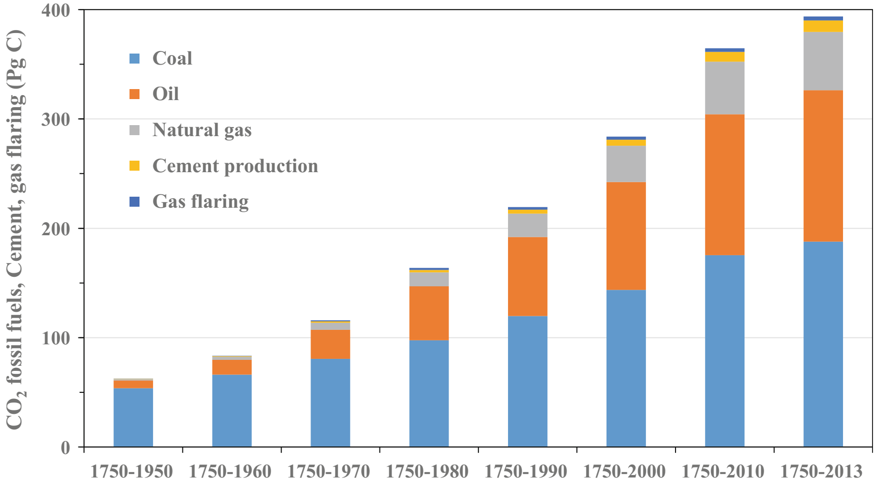
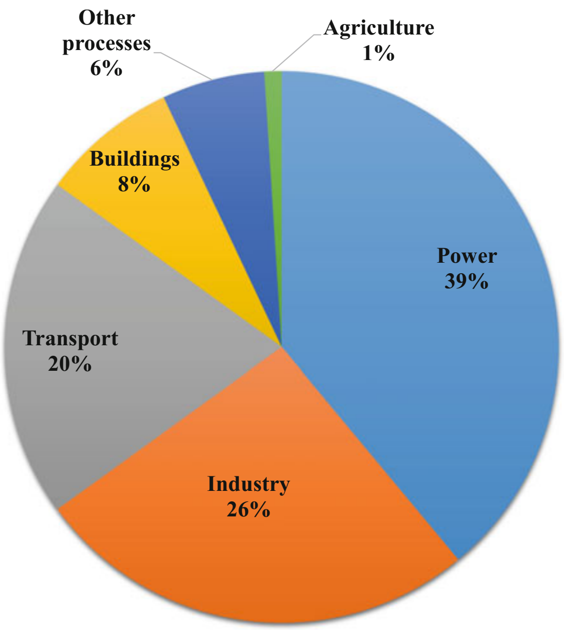


Fig. 8.1 Cumulative CO_2 emissions from fossil fuels combustion, cement production and gas flaring from 1750 showing decadal changes from 1950 to 2013

Fig. 8.2 Energy sector CO_2 emissions in 2012. *Source* IEA (2014)



Mitigation is a process of human intervention to reduce the sources or enhance the sinks of GHGs and other substances which may contribute directly or indirectly to climate change. Such substances include emissions of particulate matter that can directly alter radiation balance—such as black carbon (BC), carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic compounds (VOC), and other compounds that can alter the concentration of ozone (O_3) which can impact the climate directly. Mitigation therefore, lowers the anticipated effects on climate as well as risks of extreme impacts, and it is generally considered as part of a broader policy strategy to adapt to climate change impacts. The ultimate goal of mitigation is to prevent dangerous anthropogenic interference with the climate system within a time frame to allow ecosystems to adapt and ensure that food production and economic development proceeds in a sustainable manner.

There is a strong interest in stabilizing the atmospheric abundance of GHGs to mitigate the risks of dangerous global warming. The potential pathways to climate stabilization and/or mitigation of climate change require deployment of a broad portfolio of solutions to increase energy efficiency, replace fossil fuel use and removal of GHGs. The technological solutions available to address the challenges of increasing GHGs and the associated climate change can be broadly grouped into two: (i) non-biological solutions and (ii) biological solutions. The non-biological solutions do not involve biosphere component of natural and the managed biosphere directly, and they include techniques such as (a) reducing the global energy use, (b) establishing wind and solar farms for the power generation, (c) developing low-, C neutral, or C negative fuels, (d) capturing and sequestering CO_2 from point and non-point source and sequestration in geological formation (CCS) or capturing CO_2 from the atmosphere through enhanced natural biological sequestration or engineering techniques, and (d) geoengineering modification of climate. The biological solutions that involve biosphere components of the natural and managed C cycle include: (a) reforestation and/or afforestation, (b) sequestration of soil organic C (SOC), and (c) use of bioenergy to replace fossil fuels. Biological solutions are distinctive in two main ways: first, terrestrial and ocean C sinks already exist, and are removing more than half of the anthropogenic CO_2 emissions from the atmosphere (Canadell et al. 2007b; Canadell and Schulze 2014; Le Quéré et al. 2015), although there are some indications of sink saturation over time (Canadell et al. 2007a). Therefore, understanding and managing these sinks is important. Second, the biological mitigation approaches require enhancement of net primary productivity (NPP), followed by additional harvesting of the Earth's NPP beyond the current 38% use (Running 2012), and there are clear limits to the global fraction further available for human exploitation. The global NPP has generally remained stable at 60.2 Pg C yr^{-1} over the past 30 years with only ~ 1 Pg yr^{-1} of internal variability (Running 2012). It is estimated that 53% of global NPP is not harvestable, which includes plant growth in root systems, preserved lands, and the critical ecosystem services and biodiversity and wilderness where no transport exists for harvesting. The objective of this chapter is to present an overview of the CO_2 emission mitigation strategies.

8.2 Drivers of Carbon Dioxide Emissions

Since about 1850, global use of fossil fuels (coal, oil, and natural gas) use has increased to dominate the energy supply, replacing many traditional use of biomass fuels and also providing new services. For example, in 2009, the world used 11,161 million tons of oil equivalent (Mtoe) or 469 exajoules (EJ) of commercial energy in total, of which, nearly 90% was from fossil fuel (Larson et al. 2012). Dependency on fossil fuel has created four major challenges globally: (i) widespread lack of access to affordable alternative modern energy carriers, (ii) global climate change, (iii) global air pollution, and (iv) energy insecurity (Larson et al. 2012). Due to advantages in cost, logical maturity, and established infrastructure, fossil energy sources are likely to remain a major component of global energy supply for several decades, especially coal-based power generation and liquid gas-based hydrocarbon fuels for transport and power generation, even as the world increasingly transitions to renewable energy (RE) technologies. Increasing demand for energy comes from worldwide economic growth and development, and growing energy demand from fossil fuels plays key role in increasing trends of CO_2 emissions. This rapid rise in fossil fuels combustion (including gas flaring) has produced corresponding growth in atmospheric CO_2 burden (Fig. 8.1). Various factors have been recognized as the main drivers of increase in GHG emissions, including consumption (Hertwich and Peters 2009; Karstensen et al. 2015), international trade (Peters and Hertwich 2008;

Feng et al. 2015), population growth (O'Neill et al. 2010; Krey 2014), economic growth (Blodgett and Parker 2010), structural changes to a service economy (Nansai et al. 2009), and energy consumption (Malla 2009; Karmellos et al. 2016). While emissions from land use and land use change has increased by 12% between 1970 and 2010, the major global GHG emission have, however, been associated with CO_2 emissions from fossil energy at 108% between 1970 and 2010 (Fig. 8.1).

It has been suggested that climate change is more of an issue of economic development for both developing and developed countries than it is an environmental issue (Moomaw et al. 1999). Kaya identity provides a framework for analyzing emissions by decomposing overall changes in GHG emission into underlying factors and analyze energy related CO_2 emissions as a function of four factors: (i) population, (ii) gross domestic production (GDP) per capita, (iii) energy intensity (i.e., total primary energy supply (TPES) per GDP), and (iv) carbon intensity (i.e., CO_2 emission per TPES) (Kaya 1990, 1995) model is therefore represented by Eq. (8.1):

$$\mathrm{CO_2\,emission} = \mathrm{Population} \times \mathrm{Affluence} \times \mathrm{Energy\,intensity} \times \mathrm{C\,intensity} \tag{8.1}$$

In other words, CO_2 emissions are expressed as a product of these four factors (Steckel et al. 2011; Peters et al. 2013; Raupach et al. 2007). Overall, understanding the observed magnitudes and patterns of the factors and drivers influencing global CO_2 emissions is a prerequisite for the prediction of future climate and the Earth system changes and for human governance of climate change and the Earth system.

8.3 Options for Mitigating Greenhouse Gases Emission

The United Nations Framework Convention on Climate Change (UNFCCC) calls for stabilization of atmospheric CO_2 concentration, even though there is no agreement on what specific level of CO_2 concentration should be. The Cancun agreement calls for limiting global average temperature increase below 2 °C relative to pre-industrial (1750) temperature, and also agreed to consider a goal of 1.5 °C (UNFCCC 2010). The Copenhagen Accord also reiterated the international commitment of holding the increase in global temperature below 2 °C, and take action to meet this objective consistent with science and on the basis of equity without quantifying the degree of mitigation required to meet this commitment or assessing whether it is still possible to achieve this commitment (UNFCCC 2009). The COP 22, Climate Summit in Paris, also recommended limiting global warming to below 2 °C and making effort to limiting it to below 1.5 °C. Scenarios analysis shows that in order to be confident of achieving equilibrium temperature increase of 2–2.4 °C, atmospheric GHG concentrations would need to be in the range of 445–490 ppm CO_2 equivalent (Schneider et al. 2007; Clarke et al. 2014). This implies that global emissions will need to decrease by 50–85% below 2000 concentration levels by 2050, and begin to decrease no later than 2015 (Anderson and Bows 2011).

It is recognized that stabilization of GHG concentration will only be achieved once the rate of addition of GHGs to the atmosphere equals to the rate at which natural systems can remove them., i.e., the rate of anthropogenic emissions is balanced by the rate of uptake by natural processes such as atmospheric reactions, net transfer to oceans, and uptake by biosphere (Allen et al. 2009). The global temperature increase is, to the first order, proportional to the amount of cumulative CO_2 emitted to the atmosphere (Rogelj et al. 2015), which implies that limiting the global warming to any temperature requires annual net CO_2 emissions to be phased out to virtually zero by the time when temperature stabilization has to be achieved (Matthews and Caldeira 2008). Based on an assessment of scenarios that take into account possible evolutions of our global society, the IPCC Synthesis Report (IPCC 2014) finds that to keep warming to below 2 °C with a likely (>66%) chance, such pathways would require cumulative emissions to be limited to around 1000 Pg CO_2 after 2011 with near-zero long-lived GHGs by the end of the century (Clarke et al. 2014; IPCC 2014). A wide variety of technological options have been proposed as potential mitigation strategies reduce CO_2 emissions and stabilize the atmospheric CO_2 concentration increase, while further technological options are still being developed. However, currently there is no mitigation option that can achieve full decarbonization or C neutrality of the global economy which have been proposed. In addition, the extent of use of the proposed mitigation will mainly depend on factors including cost, capacity, environmental impact, the rate at which the technology can be introduced, and social factors such as public acceptance.

The term "carbon sequestration" is generally used to describe both natural and deliberate processes by which CO_2 is either removed from the atmosphere or diverted from emissions sources and stored in the ocean, terrestrial environments (vegetation, soils, and sediments) and geologic formations. Before anthropogenic CO_2 emissions began, the natural processes that make up the global C cycle (Chaps. 5, 6 and 7) maintained a near balance between the uptake of CO_2 and its release back to the atmosphere. However, currently the natural mechanisms of CO_2 uptake by the environmental sinks are clearly not sufficient to offset the accelerating pace of anthropogenic CO_2 emissions. This makes stabilization of atmospheric CO_2 during this century and the goal of keeping global temperature increase below 2 °C relative to the pre-industrial even a much larger challenge. The atmospheric stabilization at any concentration requires that net emission level off and eventually drops to near zero. To achieve this level of stabilization it requires transformation of energy system worldwide, which will require many decades of development and deployment. For example, during the decade of 2006 to 2015, emissions from fossil fuels, cement production, and gas flaring is estimated at 9.3 ± 0.5 Pg C, and while natural ocean and net terrestrial uptake is estimated at 5.7 ± 0.9 Pg C yr^{-1}, and land use change emissions were 1.0 ± 0.5 Pg C yr^{-1}, respectively, and 4.5 Pg C yr^{-1} accumulated in the atmosphere (Le Quéré et al. 2015, 2016). Therefore, there is a need for more direct mitigation strategies to remove 4.5 Pg C yr^{-1} (about 45% of anthropogenic CO_2 emissions) from the atmosphere, which is a central issue in consideration for the current energy and environmental policies. Large-scale application of currently known mitigation strategies together with efficient use of energy and conservation can buy time until development of new technologies can make contribution (McCarl and Sands 2007), but the ultimate goal is transformation of energy production system to C-free energy sources.

Controlling atmospheric CO_2 increase will require deliberate mitigation with an approach that combines reducing CO_2 emissions and increasing CO_2 storage both by natural C cycle and artificially created systems. Technological options for reducing anthropogenic emissions of CO_2 include (i) reducing and eventually phasing out the use of fossil fuels, (ii) substituting less C—intensive fossil fuel for more C intensive fuels, (iii) replacing fossil fuel technologies with near-zero C alternatives, (iv) enhancing the absorption of atmospheric CO_2 by natural systems, (v) capturing and safe storage of atmospheric carbon. Options which have been under discussion currently encompass atmospheric CO_2 reductions through all possible mechanisms, including deliberate carbon sequestration; use of renewable non-fossil fuels and power sources; and increased energy conservation and efficiency, among others. Of these options, only deliberate carbon sequestration currently offers the possibility of direct removal of atmospheric CO_2, through enhancement of plant growth and enrichment of soil C storage.

8.3.1 Improving Energy Efficiency

The energy supply sector is the largest contributor to the global GHG emissions. Anthropogenic GHG emissions attributed to energy supply sector increased from 13% in 1970 to about 35% in 2010 (Le Quéré et al. 2015). The annual emission growth from the global energy supply sector accelerated from 1.7% yr^{-1} in 1990–2000 to 3.1% yr^{-1} in 2000–2010 (Bruckner et al. 2014), mainly because of rapid economic growth and the associated demand for power, heat, and transport services. In addition, increased share of coal in the global fuel mix has also contributed to this trend. In 2013, the energy supply sector emitted 21 Pg CO_2 equivalents or 16.7% higher emission than those in 2010 (IEA 2015a). Reduction in fossil fuel consumption can be achieved by improving the efficiency of energy conversion, transport and use, including enhancing less energy intensive economic activities. It is estimated that 25% of energy losses are due to the distribution system conductors and cables. High voltage direct current (HVDC) transmission has the potential to reduce transmission losses and is cost-effectiveness for long aboveground lines (Negra et al. 2006). Energy conversion efficiencies have been increased in the production of electricity—for example by improved turbines, combined heating, cooling and electric power generation systems to reduce CO_2 emission further. Technological improvement in power generation have achieved gains of factors of 2–4 in the energy consumption of the vehicles, lighting, and many other appliances since 1970, further improvements and wider application of improved technologies are also expected.

8.3.2 Switching to Less Carbon-Intensive Fossil Fuels

Switching from high-C to low-C fuels can be cost-effective when suitable supplies of natural gas are available. The C emission reductions can be significant when stand-alone coal-fired systems are replaced with natural gas fired combined heat and power systems (Burnham et al. 2012). A typical emission reduction is 420 kg CO_2 MWh^{-1} for the change from coal to natural gas in electric generation, which is about 50% emission reduction (de Gouw et al. 2014). This reduction is the result of the lower carbon content of natural gas (15.3 g C MJ^{-1} compared to, e.g., 26.2 g C MJ^{-1} for sub-bituminous coal). Even higher efficiency is achieved for the combined-cycle power plants. For example, if natural gas plant is coupled with the combined production of heat, cooling, and electric power, the reduction in emissions would be even greater (de Gouw et al. 2014). This makes a substantial contribution to emission reduction from particular plant but it is restricted to plants where supplies of lower C fuels sources are available.

8.3.3 Increased Use of Low or Near-Zero-Carbon Energy Sources

Switching to renewable energy (RE) sources or nuclear power could result into deep reduction in GHG emissions. Only a small fraction of the RE has been tapped so far, and most of RE has have low lifecycle GHG emissions compared to fossil fuels. The RE sources are capable of supplying electricity, but some sources are also able to supply thermal energy, mechanical energy, as well as production of fuels that can satisfy multiple energy service needs (Moomaw et al. 2011). While there is no single dominant RE technology that can dominate energy sector at the global level, bioenergy, wind and solar energy may experience the largest global incremental growth (Fischedick et al. 2011), and the mix of RE technologies are generally dependent on local conditions, with hydropower and geothermal playing significant role in some countries. Hydropower technology is technically and economically mature, while bioenergy technologies are diverse and span a wide range of development. Examples of mature technologies include conventional biomass-fueled power plants and heating systems as well as ethanol production from sugar and starch, while lignocellulose-based transport fuels are at pre-commercial stage. Solar energy (e.g., fuels produced from solar energy) ranges from research and technological development stage to more technically mature (e.g., combined solar power). However, even the technologies that are technically mature have not reached a state of economic competitiveness.

Other RE supplies which could become commercially available include wind, biomass, geothermal, and tidal wave power depending on geographical location. The installed wind power generation is currently contributing nearly 2.6% of global energy, and is projected to contribute up to 18% of global energy by 2050 (IEA 2015b). Many of the renewable sources could make significant contributions to electric generation, as well as transportation sectors, space heating or cooling, thereby displacing fossil fuels. Many of renewable sources face constraints of cost, intermittency of supply, land use competition, and other environmental factors.

Nuclear energy is utilized for electricity generation in 30 countries around the world (IAEA 2013). Nuclear electricity represented 11% of the global electricity share in 2012 with a total generation of 2346 TWh (IAEA 2013), which is down from 17% in 1993. The growing demand for electricity, energy diversification and climate change remains a major motivation for construction of new nuclear reactors. However, the extent to which nuclear power could be applied and the speed at which its use might be increased depends on the energy industry's ability to address concerns about costs, safety, long-term storage of nuclear wastes, nuclear proliferation, and terrorism. The role of nuclear power generation is therefore, more likely to be determined by the political process and public opinion rather than the technical factors.

8.3.4 Carbon Sequestration

The process of transfer atmospheric CO_2 that would otherwise remain in the atmosphere into other long-lived C pools so that it is securely stored, or otherwise securing C pool that would otherwise be emitted to the atmosphere as CO_2 is termed as C sequestration (Lal 2008). C sequestration can be biotic or abiotic process. Biotic is performed by living organisms including plants and some microorganisms which lead to atmospheric CO_2 removal by photosynthesis and storage in biomass and soil through various biological processes. Photosynthesis occurs naturally and involves terrestrial plants as well as phytoplankton in marine ecosystems. Management intervention of both higher plants and photosynthetic microorganisms in marine ecosystems can be imposed to enhance photosynthesis and storage of OC while minimizing respiration. Such interventions include increasing use efficiency of resources (e.g., water, nutrients). Abiotic sequestration involves engineering techniques and chemical reactions that transfer atmospheric CO_2 without intervention of living organisms—plants and microorganisms. The abiotic C sequestration has received considerable attention (IPCC 2005) because of larger sink capacity than biotic sequestration. The overall objective of human-driven C sequestration process is to balance the global C budget such that economic activities result into no net gain in atmospheric C pool. Such a strategy would necessitate sequestering nearly all CO_2 generated from anthropogenic activities through long-term storage, safe, and environmentally acceptable and stable techniques with minimum risk of leakage. Some biotic and abiotic sequestration options are briefly described below.

8.3.4.1 Biotic Sequestration

Land Use and Climate Mitigation

Land use has three primary roles in mitigation of climate change: (i) C storage in terrestrial ecosystems, both in biomass and soils (ii) mitigation of non-CO_2 GHGs, and (iii) bioenergy production for offsetting fossil fuels. Land also influences mitigation through biophysical factors, including albedo. Land use is an extensive driver of global climate change. For example, from 1950 to 2005, farmland—cropland and pasture increased from 28 to 38% of the global ice-free and inland waters land area (Hurtt et al. 2011). Land is also used for variety of other purposes such as urban and infrastructure. Currently, less than one quarter of global land area shows relatively minor signs of direct human use (Erb et al. 2007; Ellis et al. 2010). Changes in land use and management results into several factors that may impact mitigation both positively and negatively. The positive impacts include (i) the demand to store C in land by reducing deforestation, encouraging afforestation and reforestation, and altering soil management practices, (ii) reduction of non-CO_2 GHG emissions by changing land management practices in favor of those practices resulting into reduced CH_4 and N_2O emissions from agriculture and also livestock production, (iii) the demand for bioenergy.

Carbon Sequestration Through Enhancement of Natural Biological Sinks

Terrestrial C sequestration involves storage of C in vegetation, both aboveground and belowground biomass and in soils, a process generally termed as phytosequestration and soil C sequestration, respectively (Post et al. 2009). In terrestrial ecosystems, C storage mainly occurs by photosynthesis, followed by C formation of biomass in the form of live and dead OM which act as a major C sinks (Lal 2008). Natural terrestrial sinks play significant role in determining the concentration of CO_2 in the atmosphere. For example, only 40% of the anthropogenic CO_2 emitted remains in the atmosphere primarily owing to natural terrestrial and ocean C sinks which sequester atmospheric CO_2 and play an important role in the global C cycle. These sinks can also be enhanced to store more C from the atmosphere. Terrestrial C sequestration include scenarios increasing C storage in arable land soils (Chap. 10), forest soils and biomass (Chap. 11), and wetlands. The C storage capacity of soil is more than the storage capacity of both vegetation and atmosphere. Therefore, a small increase in soil C provides significant effects on overall C balance of the environment. Enhancing these sinks through changing agricultural and forestry management practices could significantly improve their C storage capacity, but this may be limited by land use practice, social, and environmental factors. In addition, the storage may not be permanent, and changes in land use or management practices may release the stored C back to the atmosphere.

Terrestrial plant production is the foundation of the biosphere C cycling. Water and atmospheric CO_2 are transformed into plant carbohydrate, and this plant matter then sustains the global food web and becomes source of food, fiber, and fuel for human. The net flux of carbon from the atmosphere into green plants per unit time is defined as the net primary productivity (NPP). The global NPP range from 59.2 to 65.5 Pg C yr^{-1} (Haberl et al. 2007; Tum et al. 2016), and for more than 30 years, the global NPP has stayed near 60.2 ± 1 Pg C yr^{-1} (Running 2012), suggesting equally small global variability of the key NPP drivers of photosynthesis such as global solar radiation and total global annual precipitation. Even though there are large regional variability within the Earth system, the final totals of energy and mass flows may even out. Based on recent estimates, humans are currently appropriating about 38% of NPP (Smith et al. 2012; Running 2012), leaving nearly 62% or approximately 36.5 Pg C yr^{-1} for future available exploitation. However, 53% of the global NPP is in non-harvestable form—including plant growth in root systems, preserved lands critical for ecosystem services and biodiversity, and wilderness areas where there are no transportation exists for harvesting. Therefore, there is clear limit to the global fraction of NPP available for further human exploitation—about 10% of NPP, equivalent to 5.4 Pg C yr^{-1} (Running 2012). Currently, agriculture is consuming 38% of the global surface land and the need to exploit larger fraction of land for biomass production for climate change mitigation places this goal in direct competition with agendas for food security and biodiversity conservation, all of which require increase quantities of biomass and land to meet their goal (Smith et al. 2013). In addition, the currently emerging bio-economy which is intending to replace many of the petroleum-based products by plant-based products will further increase the demands on biomass production—and if all the remaining 5.4 Pg C yr^{-1} of NPP were to be used for bioenergy, it will only satisfy 40% of the global primary energy consumption (Smith et al. 2012) without competing for arable lands currently under agriculture a real policy dilemma if previously allocated food production for human is transformed to bioenergy production (Tilman et al. 2009).

Significant amount of C is fixed in biomass, and their dead undecomposed or partially decomposed biomass remains in soils. The biological management of C for climate mitigation has two components: (i) reduction of emissions from biological systems, (ii) increase of C storage. These can be achieved in three ways: (a) protection of existing C from loss and reduction of the current high loss, (b) replenishing of the depleted storage by restoration of ecosystems and soils, and (c) creation of new storage by afforestation or reforestation of degraded lands. Biological approach to C management offers additional benefits of biodiversity as well as ranges of other benefits including soil C stabilization, as well as local climate amelioration and recycling of waste products. Improved management of the biological ecosystems can pay dividends in terms of water and nutrients availability and restoration of degraded lands, with positive impacts on livelihoods and help in poverty reduction (Lal 2007).

Utilization of wood biomass for construction to replace cement, or biomass for replacing of fossil fuels can minimize C footprint. However, this faces the limitation that a third of the terrestrial plant production is below-ground, which is not economically harvestable, and the other third occurs on difficult or remote terrain.

Thus, there is clear natural limit to the global fraction further available for human exploitation (Running 2012).

Environmental factors such as changing climate is also exacerbating the release of biologically stored C to the atmosphere. For example, Tundra region, with low temperatures for most of the year with prolonged season of snow cover is warming up. The active layer of soil near the surface tends to be water-logged in summer and frozen in winter. Rates of OM decomposition are low and large amount of dead plant materials accumulate in the soil (approximately 218 Mg C ha^{-1}) (Amundson 2001). Tundra plants allocate most of their biomass belowground, with an estimated aboveground biomass of 40 Mg ha^{-1} (Shaver et al. 1992). Below the active layer is perennially frozen permafrost with an estimated C storage of 1600 Pg, equivalent to nearly twice atmospheric pool (Schuur et al. 2008). Even relatively small warming of the tundra can result into thawing of the permafrost which could release as much as 40 Pg C into atmosphere within four years, enough to produce nearly 20 ppm increase in atmospheric CO_2 concentration (Schuur et al. 2008).

The main mitigation involving forest, agriculture, and other land uses involve one of four important strategies: (1) prevention of GHG emissions, (2) reduction of GHG emissions to the atmosphere by conserving existing C pools in soils or vegetation that would otherwise be lost, and (3) sequestration by enhancing the uptake of C in the terrestrial reservoirs and hence removing CO_2 from the atmosphere, and (4) reduction of CO_2 emissions by substituting biological products for fossil fuels or energy intensive products. In the following chapters, the deliberate C sequestration will be discussed. Because the goal of these activities is to mitigate the rise in atmospheric CO_2, the objective of this chapter is to examine them in the context of the global C cycle fluxes and reservoirs analyzed and discussed in previous section. The overall goal of the C sequestration activities is to mitigate the atmospheric CO_2 increase. Therefore, the examination of these activities in the overall context of the global C cycle, C reservoirs, and fluxes among the reservoirs and atmosphere is needed. Summarization of estimates of potential global sequestration capacities, and description of important uncertainties and limitations will also be outlined. This information is critical to determining whether deliberate C sequestration can effectively control the increase in atmospheric CO_2 concentration. For thousands of years the C cycle remained in balance, and the atmospheric CO_2 concentrations remained fairly constant until humans began rearranging C flows, first by burning trees and plowing the land, and later, more drastically by unearthing and combusting ancient fossilized C. The fossilized sunlight (Hughes 2009) invested in C stored millions of years ago is currently combusted into CO_2 at a rate of 10 Pg C yr^{-1} or more (Peters et al. 2013; Le Quéré et al. 2015). Some of this added CO_2 is absorbed by the ocean and on the land, but only about 60%, the rest, about 40% accumulates in the air, creating a concentration that is now surpassing 400 ppm, with the implications not only for climate (Lacis et al. 2010) but also for ocean chemistry (Dupont and Poertner 2013).

After the Industrial Revolution circa 1750, and especially the last 100 years or so, combustion of fossil fuels, land use change such as deforestation, cultivation of natural grasslands, and also changes in tillage practices and other factors have perturbed the balanced C cycle, resulting into increased atmospheric CO_2 concentration. There is a consensus that increasing concentrations of GHGs in the atmosphere, particularly CO_2 and CH_4 are contributing to global climate change (IPCC 2014). The atmospheric concentrations of CO_2 and CH_4 have increased from pre-industrial levels of 280 ppm and 722 ± 5 ppb respectively (Ciais et al. 2013) to current concentrations of 400 ± 0.1 ppm and 1845 ± 2 ppb, respectively (WMO 2016). Evidence indicates that the increase in atmospheric CO_2 concentrations are the result of expanded use of fossil fuels for energy production and transportation, land use conversion, and soil cultivation. The global total cumulative CO_2 emissions from burning of fossil fuels (coal, oil and natural gas), gas flaring and cement production from 1750 to 2015 amount to 410 Pg C (Ciais et al. 2013; Le Quéré et al. 2015, 2016). In addition, since 1750, anthropogenic land use changes have resulted into about 50 million km^2 been used for cropland and pasture, corresponding to about 38% of total ice-free land area (Foley et al. 2007, 2011) compared to estimated cropland and pasture area of 7.5–9 million km^2 in 1750 (Ramankutty and Foley 1999; Goldewijk 2001). Increase in atmospheric CH_4 concentration is attributed to anthropogenic activities including extraction and processing of fossil fuels, agriculture, and the positive feedback from the global warming. Predicted increased global fossil fuel energy use imply continued increase in C emissions (EIA 2015) and corresponding rise in CO_2 and CH_4 concentrations in the atmosphere unless a major changes are made in the way energy is produced and used, particularly how C is managed (Socolow et al. 2004).

Soil C sequestration can be achieved by enhancing concentration and pools of SOC and soil inorganic C (SIC) as a secondary carbonates through land use conversion and adoption of recommended management practices in agriculture and pasture grasslands (Chap. 10) and forest ecosystems (Chap. 11), restoration of degraded and drastically disturbed soils. Majority of atmospheric CO_2 captured by photosynthesis in terrestrial plants is converted to organic matter, some of it is translocated through plant roots into soil as root exudates. Dead plant biomass is also form add OC in soils where some of it is mineralized but some is retained as SOC (Jansson et al. 2010). The efficiency of soil C sequestration mainly depends on climate, temperature, rainfall, clay content, mineralogy, moisture content, and soil texture (Metting et al. 2001). Most soils under managed ecosystems contain a lower SOC pools than their counterparts under natural unmanaged ecosystems owing to depletion of the SOC as a result of imposed management. For example, conversion of forest or natural grasslands to arable land results into depletion of 25–30% of the original SOC pool within 20–50 years of conversion (Lal 2008). For enhanced SOC sequestration, proper management of ecosystems using various RMPs as well as advanced practices to decrease SOC mineralization and CO_2 emissions are considered essential (Metting et al. 2001). These include application of biochar, perennial crops, wood burial, farming C, and various plant products (Lal 2008; Nogia et al. 2016).

Bioenergy Production

Bioenergy is energy derived from biomass, which can be deployed as solid, liquid, and gaseous fuels for a wide range of uses, including transport, heating, electricity production, combined heat and power generation, and cooking (Chum et al. 2011). The deployment of large-scale bioenergy can cause both positive and negative effects, and their deployment needs to balance a range of environmental, social, and economic objectives that may not always be fully compatible (Creutzig et al. 2015). The consequences of large-scale implementation of bioenergy for climate change mitigation depend on the: (i) technology used, (ii) location, scales, and pace of implementation, (iii) land category used—forest, grassland, marginal lands, and croplands, and (iv) business model and practices adopted and how these integrate with or displace the existing land use. Bioenergy incentive can cause cropland expansion with increased forest and other lands conversion (Reilly et al. 2012; Rose et al. 2014). How much biomass for bioenergy is technically available in the future depends on evolution of social, political, and economic factors, including land tenure and regulation, diets, and technology. Detailed discussion on the role of bioenergy in climate change mitigation is discussed in Chap. 12.

Biological Carbon Sequestration in Ocean

Several biological processes lead to C sequestration in the ocean through photosynthesis. Phytoplankton photosynthesis is one of the mechanisms which fixes approximately 45 Pg C yr^{-1} (Falkowski et al. 2000). Some of particulate organic matter formed by phytoplankton is deposited at the ocean floor and hence sequestered. Nutrients limitation e.g., Fe is one of the limiting factors on phytoplankton growth in oceanic ecosystems. Several studies have demonstrated the importance of Fe fertilization in enhancing CO_2 uptake in ocean (Falkowski 1997; Boyd et al. 2000, 2007; Boyd and Ellwood 2010). However, the topic of ocean fertilization remains debatable due to unintended consequences especially on its impacts on ocean ecosystem biodiversity (Johnson and Karl 2002; Strong et al. 2009).

The world's oceans are the primary long-term sink for human-caused CO_2 emissions, currently accounting for a global net uptake of 2.9 Pg C annually. This uptake is not a result of deliberate sequestration, but occurs naturally through chemical reactions between seawater and CO_2 in the atmosphere. While absorbing atmospheric CO_2, these reactions cause the oceans to become more acidic. Many marine organisms and ecosystems depend on the formation of carbonate skeletons and sediments that are vulnerable to dissolution in acidic waters. Laboratory and field measurements indicate that CO_2-induced acidification may eventually cause the rate of dissolution of carbonate to exceed its rate of formation in these ecosystems. The impacts of ocean acidification and deliberate ocean fertilization on coastal and marine food webs and other resources are poorly understood. Scientists are studying the effects of oceanic C sequestration on these important environments.

Overall, the lack of permanence, high costs, and the impacts on the marine biodiversity has caused the abandonment of ocean CO_2 sequestration research.

8.3.4.2 Abiotic Sequestration

Carbon Capture and Storage (CCS)

This approach involves capturing CO_2 generated by fossil fuels combustion or released from industrial sources and then storing it away from the atmosphere for very long time. A complete end to end CCS system captures CO_2 from a large stationary point sources such as hydrocarbon-fueled power plants, refineries, cement production, and steel mills. The captured flue gas is purified to obtain nearly pure CO_2, compressed for volume reduction and then transported to the injection site where it is injected into suitable deep geologic structure—typically more than 800 m below the surface. The suite of measurements, monitoring, and verification technologies are applied during the injection and post-injection to ensure the safety, efficacy and permanence of the captured and stored CO_2 and its isolation from the atmosphere (IPCC 2005; Torvanger et al. 2013). Although the concept is straightforward, in practice it becomes more complicated. CCS requires the large-scale integration of technologies for CO_2 capture, purification, compression, transport and long-term storage sites and storage of CO_2 in geological formations where it is isolated from the atmosphere for long time. The potential storage sites include depleted oil and natural gas fields and deep saline formations. Captured CO_2 can also be used for enhanced oil and natural gas recovery, although there has been ongoing debate about the quantity of CO_2 remaining stored when used for enhanced oil and natural gas recovery, however. The potential contribution of CCS technology will be influenced by factors such as cost relative to other options, the time it will remain stored, the means of transport to storage sites, environmental risks, and acceptability of this approach to the societies. CCS requires additional energy compared to similar plant without CO_2 capture. It has been recognized that if CO_2 is captured from biomass energy such as ethanol processing facilities or electricity and heat generation from biomass coupled with CCS [i.e., biomass energy CO_2 capture and storage (BECCS)] it can yield net removal of CO_2 from the atmosphere (e.g., net negative CO_2 emissions) while also generating energy, because the captured CO_2 from the biomass is that which was absorbed from the atmosphere during plant growth (Mollersten et al. 2003; Selosse and Ricci 2014; Haro et al. 2015). In the future, CCS may also contribute significantly to emission reductions from transportation sector through H_2 generation and use for light and heavy-duty vehicles, electrification of vehicles, and production of synthetic fuels from captured CO_2. The CO_2 emission reduction based on fossil fuels requires existing CO_2 sources to have retrofits, rebuilds or new units replacements, all with CCS, otherwise a new point source adding CCS would only count as avoiding increasing emissions, unless it is based on biomass or replacing existing source without CCS.

The goal of CCS is to reduce emissions from large stationary sources such as power generation plants, natural gas processing, H_2 production, and industrial sources such as cement production or steel making. CCS can reduce the emission from fossil fuels by 65–85% when fully implemented to capture all CO_2 from power generation. The remaining 15–35% are the activities occurring beyond power plant boundary which cannot be controlled through CO_2 capture. However, in reality the optimal degree of emission reduction will depend on tradeoffs between the amount of emission reduction and cost of capture and the age of facility on which CCS is deployed.

While many governments as well as organizations in the international climate and energy domains have expressed the commitment to accelerating development and deployment of industrial-scale CCS projects, engineering advances and evolution of comparative cost will influence the pace, orientation, role, and ultimate scale of CCS deployment. While CCS is framed as a bridging technology among governments and industry, the technology is contested in the environmental movement (Verma et al. 2006; Greenpeace 2008; Anderson and Chiavari 2009). Among the reasons for skepticism expressed by environmental communities include the fear that CCS will divert political attention and financial investments from renewable energy and energy efficiency, high costs of deployment, its impacts on ground water and public safety, the infrastructure expansion, and whether the technology will offer a true CO_2 lock (Kirchsteiger 2008). In general, CCS is conceived by some as a technology fix for immediate problems with long-term negative consequences (Spreng et al. 2007). The expanding literature on public acceptance and stakeholder perception of CCS reflects an awareness of deep public skepticism toward CCS technology (Huijts et al. 2007; Shackley et al. 2009; Malone et al. 2010; Johnsson et al. 2010). Detailed analysis of CCS technology is presented in Chap. 13.

Direct Injection of CO_2 into the Ocean

Injection of pure stream of CO_2 stream in ocean has been widely considered by engineers for decades (Marchetti 1977). To be stable and minimize outgassing, CO_2 must be injected at great depths, however. Although the strategy seems promising, this storage technique is hurdled by the risk of affecting the marine biota present in the vicinity of injected CO_2. The location where CO_2 is injected becomes acidic in nature because of the reduction in pH by CO_2 which is toxic to marine biota in long run, and therefore, adversely affects deep sea biota (Auerbach et al. 1997). It is believed that if liquefied CO_2 is injected at $\sim$3000 m depth could be enough for stable injection of CO_2 in ocean. Some of the problems related to the ocean CO_2 injection are the function of temperature and pressure. In addition, the environmental impact remains the most essential and controversial problem of ocean CO_2 sequestration. Elevated atmospheric CO_2 impacts phytoplankton and coral reef organisms. The rate of calcification of corals macroalgae and phytoplankton decreases with increasing CO_2 concentration in ocean (Langdon et al. 2000). Lack of systematic study to evaluate the deep sea biology and CO_2 on organisms and ecosystem is currently lacking and therefore, currently there are no projects implementing CO_2 sequestration in sea.

Mineral Carbonation

Chemical sequestration involve chemical reactions that convert atmospheric CO_2 into modified and stable compound, one of which is chemical weathering of rocks by mineral carbonation, where rocks are sources of minerals (Maroto-Valer et al. 2005). In the process of mineral carbonation CO_2 reacts with various mineral metal oxides which are present in the form of rocks leading to formation of mineral carbonates (CO_3^{2-}) which remain stable in solid rocks and so CO_2 can be stored for longer period of time (Lal 2008). Mineral carbonation reactions occur naturally as well as through industrial processes, although efficiency of the process is too low at the industrial level to have significant impact on atmospheric CO_2.

8.4 Geoengineering Options for Climate Mitigation

The ideas of climate modification have a long history (Schneider 1996, 2001; Fleming 2006). The term 'geoengineering' of climate can be traced back to Marchetti (1977) who proposed the injection of CO_2 into sinking thermohaline ocean currents to reduce the atmospheric CO_2 burden and climate change. Since its introduction, the term has evolved considerably to encompass a broad ranges of ill-defined variety of approaches that aim to intentionally alter the Earth's climate system at a large-scale (Keith 2000). The US National Academy of Science report on global warming published in 1992 included a chapter on 'geoengineering', which was defined as large-scale engineering of the environment in order to combat or counteract the effects of changes in atmospheric chemistry (NAS 1992). However, the term and the ideas it entails has not been part of mainstream climate change mitigation discussion until recently when Crutzen (2006) drew attention of the scientific and policy makers to geoengineering concepts by suggesting albedo enhancement by stratospheric sulfur injection. Since then, geoengineering concepts have grown rapidly due to increased concern about the current pace of mitigation and the projected effects of climate change. Several assessments have been conducted at national level (Royal Society 2009; Rickels et al. 2011; GAO 2011) and international level (IPCC 2012) to establish scientific basis of the techniques.

Geoengineering, also called climate engineering has been defined as a broad set of methods and technologies that aim to deliberately alter the climate system in order to diminish impacts of climate change (Keith 2000; Izrael et al. 2009; Royal Society 2009). It is a large-scale manipulation of the planetary environment to counteract anthropogenic climate change. The scale and the intent are of the central importance in geoengineering approaches to climate alteration. Whereas mitigation refers to the activities that reduce anthropogenic GHGs emission, geoengineering intervention techniques aim to mediate the effects of elevated atmospheric GHGs concentration (Keith 2000), although the distinction is not mutually exclusive, as the following discussion shows. Geoengineering is different from weather modification and ecological engineering, even though the distinction may not be clear. Over time, geoengineering emphasis has shifted from broad range of approaches to the techniques specifically directed to large scale modification of climate, generally termed as climate engineering, and in some cases these two terms have been used interchangeably (Boucher et al. 2014). Geoengineering can be divided based on the location where the interventions are carried out into: (a) land-based geoengineering, (b) ocean-based geoengineering, (c) atmosphere-based geoengineering, and (d) space-based geoengineering. The Royal Society categorizes geoengineering of the climate into two broad classes based on methodologies employed, namely: (i) solar radiation management, and (ii) the GHGs removal, particularly CO_2 to intentionally reduce the atmospheric concentrations (Royal Society 2009). Table 8.1 outlines the major differences between solar radiation management and CO_2 removal techniques. Geoengineering is a new field of research and there are relatively very few research studies focused on these approaches. Therefore, the potential role as a viable component of climate change abatement policy is yet to be determined. However, the call for research into these technologies have increased in

Table 8.1 An overview of major differences between CO_2 removal and solar radiation management proposals

CO_2 removal	Solar radiation management
• Addresses the cause of human-induced climate change, i.e., high GHG concentrations	• Do not address the cause of human induced climate change (GHGs concentrations remains unchanged)
• It does not introduce novel global risks	• Introduces novel global risks
• Currently the techniques are expensive or comparable to costs of emission reduction	• Most techniques are less expensive to deploy relative to costs of emissions reduction
• May produce only modest climate effects within decades	• Can produce substantial climate effects within years of deployment
• They raise fewer and less difficult issue with respect to global governance	• Raises difficult issues with respect to both moral and global governance
• Can be judged largely on questions of related costs of deployment	• Will be judged largely on questions related to risks
• May be implemented incrementally with limited effects as society becomes more serious about reducing GHG concentrations or slowing the GHGs concentrations growth	• Could be implemented suddenly with large scale impacts, possibly both negative and positive, even before enough research is available to understand the risks relative to inaction.
• Requires cooperation by major CO_2 emitters to have significant effect	• Could be implemented unilaterally without cooperation of major CO_2 emitters
• Abrupt termination will have limited consequences	• Abrupt termination would produce significant consequences

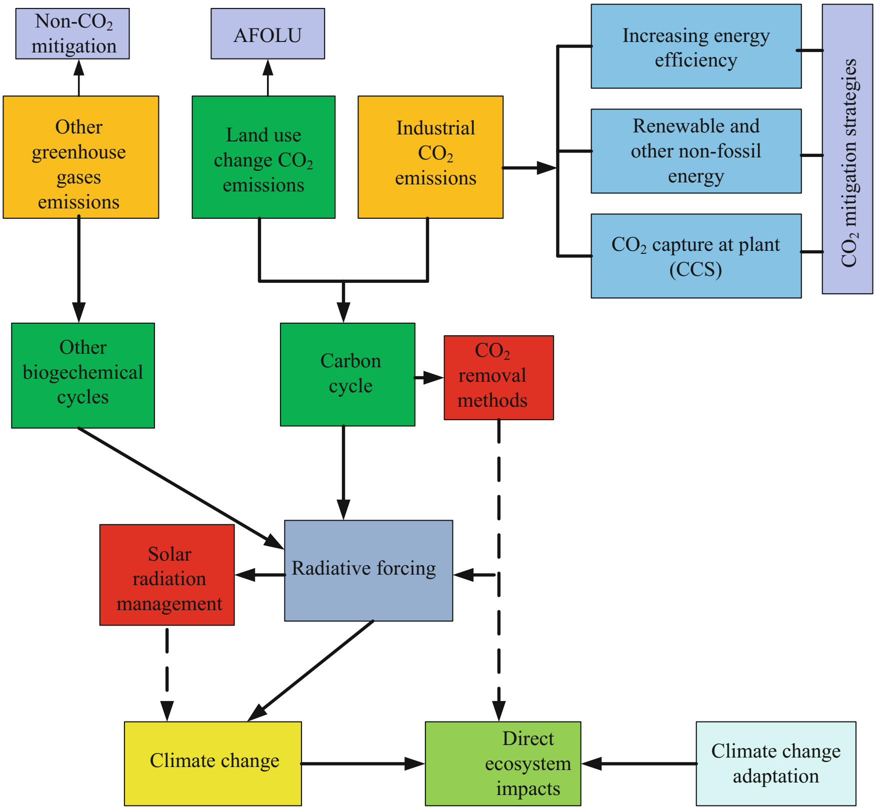


Fig. 8.3 Diagram illustrating proposed climate engineering (geoengineering) and its relationship to CO_2 mitigation methods and climate change adaptation. Adapted with modification from (IPCC 2012)

recent years (Caldeira and Keith 2010; Caldeira et al. 2013), mainly due to concerns that the pace of mitigation efforts are proving wholly ineffectual in containment of the projected effects of climate change at the global-scale due to the post 2000 trends in anthropogenic CO_2 emissions (Crutzen 2006; Canadell et al. 2007b; Cusack et al. 2014). Geoengineering approaches and their relationship with CO_2 mitigation climate change adaptation approaches are illustrated in Fig. 8.3.

In the general scientific discussions, geoengineering options have been framed in number of ways (i) as the last resort in case of climate emergence option to avoid global catastrophe (Caldeira and Keith 2010; McCusker et al. 2012), (ii) as a way of buying time for implementing conventional mitigation approaches (MacCracken 2009), and (iii) affordable fast-acting climate emergence (Caldeira and Keith 2010; Caldeira et al. 2013). Overall, most assessments agree that the geoengineering/climate engineering should not be treated as a replacement for the conventional mitigation and adaptation due to high costs involved for some techniques, and the potential risks or pervasive uncertainties involved in almost all the techniques (Royal Society 2009; Rickels et al. 2011). Two key characteristics of geoengineering methods of a particular concern are that they use or affect the climate system—atmosphere, land, or ocean—globally or regionally, and could have substantive effects that cross national boundaries. Some scientists have also argued that geoengineering could become a distraction from urgently needed implementation of mitigation measures (Preston 2013; Lin 2013).

8.4.1 Solar Radiation Management

The term SRM refers to proposed techniques aiming at intentional modification of the Earth's shortwave radiative budget with the aim of countering warming associated with increasing GHGs concentration (Keith 2000; Boucher et al. 2013). This can be achieved by reducing the amount of solar energy absorbed at the surface through increased reflection of shortwave radiation from the sun within the atmosphere or at the surface (Keith 2000). The SRM methods aim to offset global warming by reducing the incidence and absorption of incoming solar (shortwave) radiation—often referred to as insolation without reducing the atmospheric concentration of GHGs. Overall, reducing incoming solar radiation does not ameliorate ocean acidification or other negative effects associated with the increasing CO_2 concentration. In addition, successful planetary cooling would be expected to increase ocean CO_2 uptake, and therefore, amplify ocean acidification. To balance the global mean radiative forcing of $+4\ \mathrm{W\ m^{-2}}$ that would arise from a doubling of CO_2 concentration the solar management method would therefore, need to provide similar reduction in absorbed solar radiation. The solar radiation management techniques proposed include (i) placing sunshades in space—to reflect a fraction of incoming solar radiation away before it enters the Earth system or injection of stratospheric aerosols (Crutzen 2006), (ii) cloud brightening (Latham 1990), (iii) stratospheric aerosol injection, (iv) tropospheric aerosols injection, (v) settlement and crop brightening, (vi) marine cloud brightening through increased water droplet concentration, (vii) enhanced cloud albedo, and (viii) outer space reflectors (Cusack et al. 2014; Baatz et al. 2016). This list is not exhaustive, and new proposals for new solar radiation management may be put forward in the future.

Assessment of solar management methods is generally limited by (i) gaps in understanding of some important processes, (ii) a scarcity of studies evaluating their effectiveness, and (iii) scarcity of experiments using some similar designs to allow for comparison and some recommendations. Although solar radiation management geoengineering could potentially reduce the global mean surface temperature, no solar radiation management technique could fully return climate to pre-industrial or low CO_2 like climate state (Tilmes et al. 2013; Kravitz et al. 2013). In addition to its effect on planet climate, many solar radiation methods could result into serious non-climatic side effects. For example, in addition to its effects on O_3, stratospheric aerosol geoengineering would scatter light and modify optical properties of the atmosphere. The potential harmful effects of increasing atmospheric CO_2 was acknowledged as early as 1965, and suggested that bright materials spread over the oceans could solve the problem (Keith 2000). Crutzen (2006) argued that global temperature rise could be limited by injecting sulfate into the stratosphere, where it will form aerosol and reflect a fraction of the incoming solar radiation back to space, similar to phenomenon observed after large volcanic eruptions.

8.4.1.1 General Assessment of Proposed Solar Radiation Management Methods

Solar radiation management methods provide easily described mechanisms for reducing sunlight reaching the planet and they are motivation for the idealized studies based on the observed short-term cooling effect which has been observed after strong volcanic eruptions (Crutzen 2006; Sekiya et al. 2016). However, because most of known aerosols artificially injected into the stratosphere will sediment out roughly within a year or less, the aerosols requires frequent replenishment to maintain a given level of RF (Rasch et al. 2008; Kravitz et al. 2012). For example, sulfate aerosols in the stratosphere have a lifetime of $\sim$3 years, and the effect of this geoengineering method is reversed on a $\sim$3 year timescale (Vaughan and Lenton 2011). Modeling studies indicate that injection of sulfate aerosol precursors of at least 0.1 Pg S—approximately the amount of sulfur injected by the Mt Pinatubo eruption in 1991, which decreased temperature by nearly 0.5 °C for short period is needed annually to maintain $-4\ \mathrm{W\ m^{-2}}$ RF (Pierce et al. 2010; Niemeier et al. 2011). Moreover, along with potential to mitigate some aspects of global warming, many of solar radiation modification methods involving aerosols change will also increase chemical ozone loss at high latitudes and delay recovery of the Arctic ozone hole, while also increasing ultraviolet (UV) radiation reaching the surface (Table 8.2; Tilmes et al. 2012). This will also damage marine and terrestrial ecosystems. Economic and engineering consideration for the implementation is beyond the scope of this review, since little comprehensive work has been published in literature.

8.4.1.2 Technical Potential

All solar radiation management techniques require research and development before they can be implemented (GAO 2011), and also continued maintenance for long-term effectiveness. Space-based reflectors present high management challenges, while ground-based whitening solutions are limited to small areas that could be brightened. Marine cloud brightening present technological challenges for continuous suspension of water droplets. The only other technically feasible option is stratospheric aerosols. However, technical questions remains about appropriate particle size, duration of recharge, cost effectiveness, health and ecological risks, and public acceptance.

Table 8.2 Characteristics of some of proposed solar radiation management and related methods

Method	Maximum achievable radiative forcing Wm^{-1}	Risk	References
Stratospheric aerosols	Unlimited	Ozone depletion Regional drought Reduce electric generation from solar power	Bewick et al. (2012), Robock et al. (2009)
Tropospheric aerosols		Serious negative impact on human health	Vaughan and Lenton (2011)
Space-based or Earth orbit reflectors	Unlimited	Slowing of the hydrological cycle with up to 2% decrease in global mean precipitation which can be more pronounced in the tropics	Angel (2006), Vaughan and Lenton (2011)
Enhanced cloud albedo	−4		Vaughan and Lenton (2011)
Enhanced surface albedo – Grassland albedo – Crop albedo – Human settlement albedo – Deserts albedo	−4.2		Vaughan and Lenton (2011), Bala and Nag (2012), Linner and Wibeck (2015)

8.4.2 Carbon Dioxide Removal Methods

Carbon dioxide removal methods aim at removing CO_2 from the atmosphere by deliberately modifying the carbon cycle processes, or by industrial chemical approaches. CO_2 removal methods leads to net removal of CO_2 from the atmosphere while CCS only decreases the rate at which CO_2 is added to at best zero. The C withdrawn from the atmosphere can then be stored in land, ocean, or in geological reservoirs. Some of the proposed techniques involve biological processes of enhancing natural C sinks, such as large-scale afforestation and/or reforestation, C sequestration in soils through biochar, biomass energy production coupled with carbon capture and storage, and other techniques for engineering new C sinks through industrial chemical approaches. Other proposed methods involve ocean—such as ocean fertilization and alkalinity addition to the ocean. Other proposed CO_2removal processes involve geological processes such as accelerated weathering of silicate and carbonate rocks on the land or in the ocean and direct capture of CO_2 (Vaughan and Lenton 2011). Some of the CO_2 removal methods

Table 8.3 Major CO_2 removal methods, their characteristics, and potential impacts

CO_2 removal method	Cumulative potential in a century	Limitations	References
Afforestation/reforestation	40–70 Pg C	Irreversible land changes from deforestation or past land uses Decreased biodiversity Competition for the land for agricultural production	Canadell and Raupach (2008)
Accelerated weathering on land	100 Pg C	Likely increase in pH of soils and rivers Effects on terrestrial/freshwater ecosystems	Kohler et al. (2010)
Increased weathering in ocean	No determined limit	Increased alkalinity effects on marine ecosystems	Rau (2008)
Ocean fertilization	280 Pg C	Likely to cause changes to regional ocean C cycle opposing CO_2 removal Environmental consequences and potential co-benefits	Caldeira et al. (2013)
Bioenergy with CO_2 capture and storage (BECCS)	125 Pg C	Land requirement Actual amount of land available for bioenergy production is likely significantly less	Kemper (2015)
Direct air capture	No determined limit	Not known	Keith et al. (2006)
Biochar creation	130 Pg C	Alteration of surface energy budget Localized surface warming or cooling Change in hydrological cycle	Woolf et al. (2010)
Enhanced upwelling to bring more nutrient to surface waters of oceans	1–2 Pg C	Causes changes to regional ocean C cycle opposing to CO_2 removal	Lenton and Vaughan (2009)

(Table 8.3) include: (i) bioenergy with carbon capture and storage (BECCS), (ii) biochar production and application in soils, (iii) ocean fertilization by adding limiting nutrients to surface waters, (iv) land based increased weathering by application of ground silicates to soils, (v) ocean-based increased weathering, (vi) direct air capture, and (vii) large-scale afforestation and reforestation, among others. Some methods that fall under CO_2 removal are also regarded as mitigation measures. Sometimes, the term “negative emission technologies” is used as an alternative to CO_2 removal methods (McGlashan et al. 2012; Tavoni and Socolow 2013; Tokarska and Zickfeld 2015), which can also be grouped into industrial technologies versus ecosystem manipulation. However, these categorizations do not capture all geoengineering options which have been proposed, and various studies have compiled and evaluated different schemes (Vaughan and Lenton 2011; Keith 2000; Boyd 2008; Feichter and Leisner 2009; Boucher et al. 2014; Zhang et al. 2015). Overall, all CO_2 removal methods have similar slow impact on the rate of warming as mitigation measures. Permanence of the stored CO_2 in the C reservoir is the major key towards the consideration for the efficacy of any CO_2 removal methods. In addition, the effect of many of the CO_2 removal techniques will decrease over time, due to response of land and ocean C reservoirs to ongoing atmospheric perturbations associated with continuation of anthropogenic GHG emissions. In the long-term, the only way to return atmospheric CO_2 concentration to pre-industrial levels is to permanently store an amount of CO_2 equivalent to the total emission to the atmosphere into crust, sediments, ocean, and terrestrial biosphere in some form of combination.

8.4.2.1 Land Carbon Sink Enhancement

Overall, more C was stored on the land in the pre-agriculture and pre-industrial state than today (Prentice et al. 2011). Therefore, there is clearly some potential to enhance the land carbon sink by increasing land C storage, with the majority of C storage potential in soils (Batjes 1996). The estimated long-term potential for increasing conventional vegetation and soil C storage is estimated to be ~ 190 Pg C by assuming the reversal of all cumulative land-use change emissions to date (Le Quéré et al. 2015, 2016), which is equivalent to a long-term radiative forcing of ~ -0.24 W m^{-2} (Lenton and Vaughan 2009). Among the proposed land C sink enhancement are large-scale afforestation and reforestation, biochar production and application to soils, and BECCS. However, the general concern is that a large-scale afforestation and reforestation for increase in C storage on the land most likely would conflict with food production requirements to feed the increasing global population, unless sustainable intensification of existing agricultural lands can increase productivity and reduce the land area appropriated to food production (Lal 2016).

The conversion of land from non-forested to forested land is termed afforestation if the land has been without trees for >50 years, or reforestation if trees were lost in the last 50 years, and is currently considered as one of the mitigation options, although afforestation and reforestation have been included as geoengineering method due to the potential for negative CO_2 emissions. The large-scale afforestation tends to decrease the local land surface albedo and increase the adjacent regional surface air temperatures. This kind of albedo change may result in more warming than if no large-scale afforestation or reforestation was implemented (Keller et al. 2014). In some locations, this can outweigh the radiative forcing effect of enhanced C storage (Betts 2000). Forest cover also tends to enhance cloud cover and reflectivity through increasing evapotranspiration. Generally, in the tropics afforestation exerts a net cooling, while in the temperate regions the net effect is a marginal cooling and in high latitudes with seasonal snow cover afforestation is counterproductive (Bala et al. 2007).

Biochar is produced by the pyrolysis of the biomass (i.e., combustion of biomass in the absence of O_2). It can be produced as a byproduct of bioenergy production (Lehmann et al. 2006). When applied into the soils, biochar acts as a recalcitrant C reservoir and it can be used to increase land C sink. The long-term global storage potential for croplands and grasslands has been estimated at 224 and 175 Pg C, respectively, with a potential radiative forcing offset of ~ -0.52 W m^{-2} (Vaughan and Lenton 2011; Lenton and Vaughan 2009). However, the process of producing biochar involve additional energy penalty which brings additional CO_2 emissions. The more extensive bioenergy to replace fossil fuels results in C neutral energy production, and if CO_2 is captured and stored through geological sequestration, the process becomes C-negative. Therefore, BECCS amounts to creating a new C sink on land with potential economic benefits compared to CCS. BECCS can be applied to a variety of biofuel production pathways based on biomass, including forestry products, sugar cane, switchgrass, miscanthus, ethanol production from food products followed by capture and storage of the CO_2 produced in the fermentation process and in combustion at the power stations. Scientists have also suggested decreasing the amount of CO_2 emitted from a corn-based ethanol biofuel through the cultivation of microalgae (Rosenberg et al. 2011).

8.4.2.2 Bioengineering

The bioengineering approach involves engineering climate because of the albedo differences between plants (Ridgwell et al. 2009) or land cover type. In agriculture, crop plants have higher albedo than natural vegetation. Also different varieties of the same crops could have different albedo. The bioengineering could involve a change in variety of crops grown, which may not affect food production. Modeling assessment of impact of crop albedo bioengineering showed that increasing crop canopy albedo by 0.04, representing a potential increase of 20%, produces the cooling as large as 1 °C during summer time in Europe with greater cooling in South East Asia (Singarayer et al. 2009). The relatively low implementation costs of crop albedo bioengineering makes it potentially attractive compared to other geoengineering proposals (Ridgwell et al. 2009).

8.4.2.3 Accelerating Chemical Weathering on the Land

Silicate rocks are the most common rocks on Earth, and their weathering reduces atmospheric CO_2 concentration and also governs atmosphere—soil CO_2 uptake over geological timescales. Geoengineering proposal for artificially increasing weathering of silicate minerals include decomposing river chemistry into rock weathering products (Schulte et al. 2011).

8.4.2.4 Ocean Carbon Sink Enhancement

Oceans covers 70% of the Earth's surface and contains approximately 50 times more C in the surface layers than the atmosphere. Therefore, ocean-based geoengineering have large potential for CO_2 removal. Overall, the natural pre-industrial state of C cycle had an excess of C in the deep ocean relative to surface and atmosphere. The solubility pump where surface waters move from low to high latitudes, cooling, and absorbing CO_2 before sinking to depth has been responsible for maintaining the disequilibrium. The exchange of C between surface oceans and atmosphere is estimated to be 90 Pg C yr^{-1} for the 2010s (Ciais et al. 2013; Le Quéré et al. 2015, 2016), and the net annual effect of oceans is currently a C sink of 3.0 ± 0.5 Pg C yr^{-1} (Le Quéré et al. 2015, 2016). The present ocean C sink is driven by an anthropogenic excess of CO_2 in the air relative to the sea. The majority of the extra CO_2 entering the surface ocean is transported to depth by the solubility pump. The proposed climate geoengineering processes in the ocean attempts to enhance the elements of existing ocean sink. These include: (i) enhancing the solubility pump, and (ii) enhancing biological pump. The effectiveness of these techniques depends on successful transport of C to depth. The return timescale of C that is remineralized at different depths in the ocean is generally dictated by the movement of water masses and it can range from weeks to millennia. Detailed understanding of where remineralization is occurring within water column and the specific dynamics of water masses downstream of the targeted region is also required.

The proposed methods for enhancing the solubility pump focuses on increasing the absorption of CO_2 in the surface waters by increasing the sinking CO_2-rich waters or manipulating surface water chemistry (Zhou and Flynn 2005; Harvey 2008; Zhang et al. 2015). These include: (i) increasing downwelling, and (ii) increasing ocean alkalinity. Increasing downwelling can be achieved by cooling surface waters. However, the combination of high costs and uncertainty of the effectiveness limit this approach (Zhou and Flynn 2005). The alkalinity of the oceans can be increased through the addition of carbonate minerals (Harvey 2008). This engineered pH lowering technique exploits the ocean C chemistry, and will allow more anthropogenic CO_2 to be absorbed. The use of $CaCO_3$ which is found in abundance in the form of limestones, but can be processed to more soluble form into lime (CaO) has been advocated (Kheshgi 1995). However, mining substantial volumes of limestone can have a localized environmental impacts on mined land area. Also taking into consideration the energy costs of mining and processing limestone together with land and marine transportation will outweigh the benefits of this engineering process (Harvey 2008).

The proposed geoengineering for enhancing the biological pump involve enhancing export production by either directly adding limiting nutrients to the ocean surface (Lampitt et al. 2008) or by mechanically enhancing upwelling of nutrient-rich water from below (Karl and Letelier 2008). Specific proposals include: (i) iron fertilization (Jin et al. 2008), (ii) macronutrient fertilization, and (iii) enhancing upwelling (Lampitt et al. 2008; Caldeira et al. 2013). Several iron fertilization experiments have been conducted, majority in the Southern Ocean (Boyd et al. 2007; Lampitt et al. 2008). Based on experimental data and modeling, it is estimated that, on millennial timescale, the extra C that could be stored in the deep ocean through alleviating iron limitation range from 106 to 227 Pg C (Aumont and Bopp 2006). It has also been suggested that there is deficit of available N relative to P in the world ocean of an average 2.7 μmol kg^{-1} (Anderson and Sarmiento 1994), and removing the N deficit would result in a ~9% increase in export flux (Vaughan and Lenton 2011). However, plans to do macronutrients fertilization have been met with strong concern, resulting in memorandum issued by the United Nations Convention on Biodiversity that called for large-scale fertilization attempts to be prohibited. Overall, enhancing the biological C pump is a limited short-term climate engineering because the total export production from the surface layers of the global oceans is low, ~10 Pg C yr^{-1} and cannot be greatly increased (Vaughan and Lenton 2011). Therefore, enhancing primary production in the surface layer of the ocean does not directly translate into an equivalent long-term sink of CO_2, since most of the C fixed in the surface layer of ocean are recycled within the surface waters and degassed back to the atmosphere.

8.4.2.5 Direct Air Carbon Dioxide Capture and Storage

Direct air CO_2 capture refers to the chemical process by which a pure CO_2 stream is produced by capturing CO_2 from ambient air. The captured CO_2 could be sequestered in geological reservoirs or in deep ocean. Three methods have been proposed to capture CO_2 from the atmosphere: (i) adsorption on solids (Lackner et al. 2012), (ii) absorption into highly alkaline solution (Keith 2009; Mahmoudkhani and Keith 2009), and absorption into moderate alkaline solution with catalyst (Bao and Trachtenberg 2006) Using chemical engineering methods, CO_2 can be removed from the atmosphere using sorbent materials such as NaOH which selectively traps CO_2 (Keith et al. 2006). The sorbent can then be regenerated and reused. Direct air CO_2 capture is generally limited by thermodynamic barrier due to low concentration of CO_2 in ambient air.

8.5 Conclusions

The Earth has entered a period in which climate is changing more rapidly than ever experienced in recorded human history, primarily caused by rapid increase in atmospheric GHGs concentrations. As a result, global surface temperature is projected to rise over the 21st century under all assessed emission scenarios. Other changes include longer and more frequent heat waves, more intense extreme precipitation events, warmer and acidified oceans, and global sea level rise. The two main options for responding to risks of climate change involves mitigation, i.e., reducing and eventually eliminating human-caused emissions of CO_2 and other

GHGs, and adaptation i.e., reducing the vulnerability of human and natural ecosystems to changes in climate. Mitigation would require substantial reduction of anthropogenic GHGs to near zero over the next few decades. Implementing such reductions poses substantial technological, economic, social, and institutional challenges, and these challenges increases with delayed implementation of mitigation strategies. Some of the mitigation strategies discussed in the next chapters are decabonization of energy supply, reduction of net GHGs emission, enhancing biological C sinks in land based sectors and CO_2 capture and sequestration. A third potentially viable option been considered by scientific community involves climate engineering techniques generally referred to as geoengineering. Scientific discussion on research on geoengineering has currently become more acceptable than few years ago, and Intergovernmental Panel on Climate Change in their fifth assessment (IPCC AR5) devoted several sections on geoengineering of the climate, mostly due to lack political will to implement serious mitigation, living the geoengineering of climate as available choices to avoid catastrophic abrupt climate change. Overall, the general public seems to be opposed to SRM and some of CDR schemes research at present, mostly due to the fears of risks associated with unintended consequences, which may have impacts on human health, ecosystems, and biodiversity. Current geoengineering assessments have mostly focused on physical science aspects, while assessments on law, governance, economics ethics, and social policy of geoengineering is limited. Also, despite various assessments of their potential, geoengineering ideas are still far from deployment-ready. The drawbacks of SRM geoengineering methods remain large, and not easy to overcome, even though the SRM methods can act rapidly to mitigate the global temperature rise. Unwanted side-effects such as diminished rainfall in some regions which could occur alongside the intended effects, among others may limit scientific research on SRM. Importantly, once started, SRM geoengineering must be maintained for very long period, otherwise, when it is terminated, climate reverts rapidly to maintain global energy balance. Therefore, evaluating potential effectiveness, risks, and climate feedbacks of different geoengineering methods become important for governing large-scale field experiments.

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Chapter 9
Introduction to Terrestrial Carbon Sequestration

Abstract From the industrial revolution in 1750 to 2015, about 600 Pg C have been released by human activities into the atmosphere as carbon dioxide (CO_2). Atmospheric measurements indicate that about half of the emitted CO_2 remains in the atmosphere, while the ocean and terrestrial sinks have been removing the remaining half at a steadily increasing rate. Due to direct and indirect anthropogenic perturbation of the biosphere, the atmospheric concentration of well-mixed greenhouse gases-CO_2, methane (CH_4) and nitrous oxide (N_2O), has increased from pre-industrial revolution concentrations of 278 ppm, 700 ppb, and 270 ppb for CO_2, CH_4 and N_2O, respectively to a global abundances of 400 ppm, 1845 ppb and 328.1 ppb for CO_2, CH_4, and N_2O, respectively in 2015. The mean annual absolute atmospheric increase during the last ten years was 2.06 ppm, 4.7 ppb, and 0.87 ppb yr^{-1}, for CO_2, CH_4 and N_2O respectively. Carbon stored in global soils exceeds the amount of C stored in plant biomass and atmosphere and represent a large component of C cycle that may participate in climate change feedbacks, especially on decadal and centennial timescales. In addition to loss of stored carbon (C) associated with anthropogenic activities, losses of SOC due to climate change could also contribute to increasing atmospheric CO_2. Loss occurs through heterotrophic respiration, and is dependent on temperature, moisture, and disturbance regimes including land use change and fire. Because soil is the basic resource in agriculture, grassland and forest land use, it is the central component of most sustainable land management technologies. Soil C has a direct correlation with soil quality, and it is a major determinant of soil's ability to hold and release nutrients that are essential for plants and their root system. Terrestrial C sequestration, a process by which atmospheric carbon dioxide (CO_2) is taken up by plants through photosynthesis and eventually stored as C in the biomass and soils, can have significant impact on mitigation of climate change by limiting CO_2 concentration in the atmosphere, while also reversing the soil fertility loss in agricultural ecosystems. Land-based biological C mitigation strategies are viable pathway toward climate stabilization.

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Keywords Phytosequestration · Fossil fuel emissions · Soil carbon sequestration · Land use change · Global carbon cycling · Pedologic carbon pool

Contents

9.1 Introduction

Carbon (C) is an essential element for sustaining life. It is found naturally in organic and inorganic forms in all living organisms, with a small exchange rate between organic and inorganic forms. The C concentration of living matter is 18% (about 50% on dry basis), which is almost 100 times greater than average concentration in the Earth—estimated at 0.19% (Schlesinger 1997). Thus, for life to continue, C must be recycled. The recycling of C is generally accomplished primarily by photoautotrophs that use light energy from the sun to convert atmospheric carbon dioxide (CO_2) to organic C by photosynthesis. This C is returned to the atmosphere as CO_2 by respiration, organic matter decomposition, and combustion. Therefore, C atoms circulate unhindered within and among ecosystems, traversing all arbitrary boundaries of space and time. This endless cycle of C had been more or less balanced for many millennia until human beings began interfering with the natural flows—first by forest clearing and burning trees and plowing the land for crop production, then more drastically by unearthing fossilized C and bringing it into circulation through burning of fossil fuels and release of CO_2 to the atmosphere at an increasing rates annually. Decadal CO_2 emissions from fossil fuel combustion increased from 3.1 ± 0.2 Pg C yr^{-1} in 1960–1969 to 9.3 ± 0.5 Pg C yr^{-1} in 2006–2015. In contrast, decadal land use emissions declined from 1.5 ± 0.5 Pg C yr^{-1} to 1.0 ± 0.5 Pg C yr^{-1} over the same period (Le Quéré et al. 2015, 2016). As a result of emission increase, ocean and terrestrial C sinks also increased from 1.2 ± 0.1 and 1.7 ± 0.7 Pg C yr^{-1} in 1960 to 1969, respectively to 4.5 ± 0.1 and 3.1 ± 0.8 Pg C yr^{-1} in 2006 to 2015, respectively, while the remaining C remained in the atmosphere, resulting into atmospheric CO_2 concentration growth at 1.7 ± 0.1 Pg C yr^{-1} in 1960s to 4.5 ± 0.1 Pg C yr^{-1} in 2000s (Le Quéré et al. 2015, 2016), with implications not only to climate, but also for the ocean chemistry which absorbs about one third of the anthropogenic C.

For thousands of years, the cycling of C remained nearly in balance, and the atmospheric CO_2 remained fairly constant. However, since the beginning of the

Industrial Era in 1750, deforestation, changes in land use, combustion of fossil fuels, and other anthropogenic activities have perturbed this balance, resulting in increase in atmospheric CO_2 concentration. Similarly, agriculture and livestock, as well as fossil fuels production have increased anthropogenic emissions of CH_4, while agriculture, especially the use of N fertilizers in crop production are responsible for anthropogenic N_2O emissions. Since 1950s, oceans and terrestrial ecosystems have taken up a net, about 45% of all fossil fuel emissions, with remaining net of about 55% retained in the atmosphere (Canadell et al. 2007b). The cumulative atmospheric growth rate from 1750 to 2015 is estimated at 260 ± 5 Pg C (Table 9.1), at an average increase of 0.96 and 4.3 Pg C yr^{-1} between 2002 and 2011 (Ciais et al. 2013). There are indications that the fraction of net anthropogenic CO_2 taken up by the oceanic ecosystems is decreasing (Le Quéré 2010; Lovenduski et al. 2015; Le Quéré et al. 2010), indicating that natural sinks may not be able to keep pace with the ever increasing anthropogenic CO_2 emissions. Since the beginning of industrial era, the atmospheric CH_4 has increased by 2970 ± 47 Tg, at an estimated growth rate of 11 Tg CH_4 yr^{-1} and 17 ± 9 Tg yr^{-1} between 1990 and 1999. Similarly, the atmospheric N_2O has increased by 213 ± 50 Tg, at an average decadal atmospheric increase of 0.73 ppb yr^{-1} or 0.81 ± 0.15 Tg N_2O yr^{-1} (Ciais et al. 2013).

Although thermogenic sources (i.e., fossil fuel combustion and usage, cement production, geological and industrial processes) represent the single largest perturbation of climate forcing, biogenic sources and sinks also account for significant proportion of land-atmosphere exchange of greenhouse gases (GHGs). Land biogenic GHG fluxes originate from plants, animals, microbial communities with changes driven by both natural and anthropogenic perturbations (Tian et al. 2016). Increasing levels of atmospheric GHGs, particularly CO_2, and failure of environmental sinks to keep pace with increasing anthropogenic GHG emissions are contributing to global climate change (IPCC 2007, 2014). The atmospheric CO_2 concentration has increased significantly from the preindustrial concentration of 278 ppm to nearly 400 ppm in 2015 (WMO 2016), and the evidence indicates that the increased concentrations are the result of combination of combustion of fossil fuels for energy production and transportation, deforestation and land use conversion, and soil cultivation. Increased energy demand to meet future demands for

Table 9.1 Current atmospheric greenhouse gases burden, cumulative emissions and average annual emissions during 1750 and 2014 (Ciais et al. 2013; Le Quéré et al. 2015, 2016)

Greenhouse gas	Atmospheric burden	1750–2015	
		Cumulative atmospheric increase	Average atmospheric increase
Carbon dioxide (CO_2) Pg C	844 ± 10	260 ± 5	4.0 ± 0.1
Methane (CH_4) Tg CH_4	4954 ± 45	2979 ± 45	17 ± 9
Nitrous oxide (N_2O) Tg N_2O	1553 ± 50	213 ± 50	3.6 ± 0.15

energy and also increased food production to meet the demand for increasing population imply continued increase in CO_2 emissions and the corresponding rise in atmospheric CO_2 unless the major changes in energy sources, and in particular, how C is managed is implemented (Socolow et al. 2004; Greenblatt and Sarmiento 2004).

Although terrestrial biosphere, ocean, and atmosphere are reservoirs of C, and CO_2 naturally circulates and accumulates in these reservoirs as part of the natural C cycle, the natural land biosphere and oceans are unable to absorb all of the anthropogenic CO_2 currently being emitted. As a result, residual anthropogenic CO_2 is currently accumulating in the atmosphere at a projected rate of 6.3 ± 0.2 Pg C yr^{-1} for 2015 (Le Quéré et al. 2016). Therefore, there is a need to enhance natural C pools and to artificially provide new C sinks to offset the atmospheric CO_2 accumulation. One option which has received considerable attention is the terrestrial C sequestration, which transfers atmospheric CO_2 into biotic and pedologic C pools and occurs when natural uptake of C by plants and soils exceeds losses through plants and soil respiration and biomass removal. Therefore, terrestrial sequestration stores CO_2 in vegetation and in soils, in the above ground and below ground biomass, a process termed as phytosequestration and soil C sequestration, respectively (Post et al. 2009). In terrestrial ecosystems, C storage mainly occurs through photosynthesis as well as in the form of live and dead organic matter (OM), hence acting as major C sinks in terrestrial ecosystems (Lal 2008). Terrestrial ecosystems provide the active mechanisms for biological removal of CO_2 from the atmosphere through photosynthesis and play an important role in the global C cycle. The sustainable potential of land-based C sequestration requires addressing the dilemma of how to meet demands for climate change, energy security, food security, and biodiversity conservation at both regional and global scales. Specifically, soil management needs to address the following: (i) increase food production to feed a growing and more affluent population, (ii) increase C sinks to reduce excess atmospheric CO_2, (iii) produce energy from biomass to increase energy security while also reducing the dependence on fossil fuels, (iv) reduce human encroachment into native ecosystems to minimize anthropogenic CO_2 emissions. In addition, there is a need to reduce anthropogenic GHG emissions from combined human activity to near zero if climate stabilization is to be achieved (IPCC 2014).

Photosynthesis by plants is able to capture and remove CO_2 from the atmosphere and convert it to OM and act as reservoir of photosynthetically-fixed C through storage in various forms in plant tissues, both living and dead. Some of the captured C returns to the atmosphere through decomposition of OM or combustion of biomass, but some of it can remain in soils or in plant tissues for many years. By changing land management practices, the amount of C stored in soils and plants can be increased and offset some of CO_2 accumulation in the atmosphere. Storing C this way is referred to as terrestrial C sequestration or sequestration through natural biological processes. In addition to being safe natural process of storing C, it has advantages that it can be quickly instituted and has the ancillary benefits such as increased crop yields, improved soil water retention, and improved wildlife habitat, among others. Terrestrial C sequestration with the application of known best management practices could conservatively sequester more than 0.5 Pg yr^{-1} by 2040, contributing 6–23% of emissions mitigation by as much as 40 Pg C by 2100 (Thomson et al. 2008; Obersteiner et al. 2010).

Varieties of options for terrestrial C sequestration include restoration of degraded lands, restoration of mined lands, afforestation, reforestation, rangeland improvement, improved tillage practices, and wetland restoration. Planting trees in cleared areas and abandoned farmlands instead of grass increases C storage per hectare, since forests contain more C per hectare when taken into account the amount of C stored in wood. The objective of this chapter is to describe the land management techniques for enhancing terrestrial C sequestration as one of the climate change mitigation options and outline the approaches for quantifying changes in both biomass and soil organic C (SOC).

9.2 Terrestrial Carbon Pools

Although there is a considerable debate about the amount of C stored and emitted from terrestrial ecosystems (van der Werf et al. 2009; Harris et al. 2012; Le Quéré et al. 2015), there is a consensus that large quantity of C is held in word soils, and the emissions from land use and land cover change are the second largest anthropogenic source of C to the atmosphere after emissions from fossil fuel combustion (IPCC 2014). In view of the large quantity of C held as OM in world's soils, it is entirely appropriate to consider how its management might either mitigate or worsen climate change. It is estimated that the global pool of SOC in the range of 684–724 Pg C is stored in the top 30 cm depth of the world soils (Batjes 1996; Jobbagy and Jackson 2000; Hiederer and Köchy 2011; Scharlemann et al. 2014). The quantity of SOC in the 0–30 cm layer is nearly the same as the amount of C in the atmosphere as CO_2 and that in the global above ground vegetation (Ciais et al. 2013). Because of large quantities of organic C held in world's soils, small change in this large stock of SOC could have significant impacts on the future atmospheric CO_2 concentrations. If the SOC stock declines due to management practices or impacts of climate change, it means additional CO_2 will be released into atmosphere, adding to future climate change. In contrast, if management practices that can cause SOC to increase over large land areas are implemented, it could be an important means of slowing the current increase in atmospheric CO_2 concentration and contribute to mitigating the climate change. Different forms C and their sources are summarized in Table 9.2. CO_2 emission from terrestrial C pools is a function of: (i) the amount of C in biomass and soils (i.e., C stocks), (ii) the spatial distribution of C stocks, and (iii) impacts of land management on plant and soil C stocks. Models that have coupled climate and C cycle show a large divergence in size of predicted biosphere feedback to the atmosphere (Friedlingstein et al. 2006; Todd-Brown et al. 2013), and several questions which still remain when attempting to reduce this uncertainty in response of soils to climate change are:

Table 9.2 Forms of carbon in the soil

Carbon forms	Source
Elemental C	• Geologic materials (e.g., coal and graphite) • Incomplete combustion of organic materials (e.g. charcoal, soot, and graphite) • Dispersion of these sources during mining activities
Inorganic C	• Geologic or soil parent materials, usually as carbonates—calcite, $CaCO_3$, dolomite, $CaMg(CO_3)_2$, and siderite $FeCO_3$ • Agricultural inputs such as liming, which can introduce calcite and dolomite into the soil
Organic C	• Plant and animal materials at different stages of decomposition ranging from crop residues, with the size of 2 mm or more • Plant debris generally referred to as particulate organic C with size between 0.05 and 2 mm • Highly decomposed materials less than 0.05 mm that are dominated by molecules attached to soil minerals

(i) temperature-sensitivity of SOC, especially of the more recalcitrant pools, (ii) the balance between increased C input to the soil from increased plant production and increased losses due to increased rates of decomposition, and (iii) interactions between climate change and other aspects of global change including other climatic effects—change in water balance, changes in atmospheric composition, i.e., increase in atmospheric CO_2 concentration, and land use change. The uncertainty in modeled estimates of soil C remains very large (Todd-Brown et al. 2013), probably due to uncertainties in the input data, type of model input used (e.g., net primary productivity (NPP), temperature) as well as resolution of the models (Todd-Brown et al. 2013).

Climate change is likely to influence both the quantity and quality of C entering soil from plant inputs and also its rate of decomposition. For example, an increase in atmospheric CO_2 is likely to increase plant productivity and therefore, C inputs from plant litter and roots, though plant growth will also be influenced by temperature and water availability, and these influences could either be positive or negative in different regions depending on whether climate change relieves current constraint to growth or imposes a new constraint. Therefore, in the following chapters, the key factors to be addressed are (a) what management practices or changes in land use which tend to release additional C from soil should be avoided? (b) What management practices or changes in land use which tend to increase SOC stock either by slowing SOC decomposition or through increased atmospheric C input to soils through plants and thus should be encouraged as a climate change mitigation measures, and (c) how is the current SOC stock likely to be influenced by climate change? These includes consideration of impacts of increase in temperature, increased CO_2 concentration and changes in soil moisture regimes resulting from climate change.

9.2.1 Carbon Losses from Soil

Converting land of high SOC content, such as forest or grassland, to arable land use will generally lead to a loss of SOC and emission of additional CO_2 to the atmosphere. Another land use change with serious consequences for SOC stocks, and hence for increased emissions of CO_2 to the atmosphere is drainage of peat soils. Peatlands cover about 4.16×10^6 km^2 worldwide, and 80% of the peatland area situated in temperate-cold climates in the northern hemisphere, particularly in Russia, Canada and the USA, and the remaining peatlands are found in tropical-subtropical climates, particularly in south-east Asia (Limpens et al. 2008). Despite occupying less than 3% of global land surface, these soils hold vast stores of C. For example, boreal and subarctic peatland store between 270 and 370 Pg C (Limpens et al. 2008), while tropical peatland C stores are estimated to be around 52 Pg C, with very large uncertainties 8–258 Pg C (Hooijer et al. 2010). Global estimates of C stored in peatland and wetlands range from 300 to 700 Pg C (Bridgham et al. 2006). The C pool size in North American wetlands (Canada, USA, and Mexico) is estimated at 215 Pg C, and current C sequestration rate in these wetlands is ~ 57 Tg C yr^{-1} (Bridgham et al. 2006). Drainage of these soils leads to large amounts of SOC losses that continue for hundreds of years. One of the current examples of peatland drainage is the tropical peatland drainage to grow additional oil palm for production of biofuels. After drainage and conversion to more aerobic conditions, peat oxidizes at an increased rate leading to greatly increased emissions of CO_2 for decades or even longer. It is estimated that CO_2 emitted after clearance of peatland rainforest of Southeast Asia to grow oil palm for biofuel production would outweigh the GHG benefit from biodiesel replacing fossil fuel for over 400 years and termed this as carbon debt (Fargione et al. 2008). In addition, lowland coastal peatlands C storage is also vulnerable to sea level rise (Whittle and Gallego-Sala 2016).

9.2.2 Terrestrial Carbon Sequestration

Terrestrial C sequestration, sometimes termed as “ecological” or “biological” C sequestration refers to the process of transferring atmospheric CO_2 that would otherwise remain in the atmosphere into long-lived terrestrial C pools—plant biomass and SOC, or retaining C that is stored in terrestrial C pools such as biomass C and SOC in long term storage (Lal 2008). Terrestrial C sequestration can also occur through inorganic C storage in soils and water through carbonate ($CO_3{}^{2-}$) formation, a sequestration process that becomes important at geological timescale (Monger et al. 2015). Inorganic C pool in global soils is estimated at ~ 940 Pg C to 1-m depth, and is mostly as $CO_3{}^{2-}$ (Monger et al. 2015). Terrestrial SOC sequestration occurs naturally through photosynthesis where C is stored in biomass, and some of the biomass C can also be transferred and stored as SOC. It can also be enhanced by anthropogenic processes through best management practices (BMPs) in agriculture and grasslands (Chap. 9) and forest (Chap. 10). Terrestrial ecosystems also provide a flow of harvestable products that contain C and compete in market place with fossil fuels, and other purposes that also has implications for global C cycling (Chap. 12).

The C stored in soil and forest biomass can persist for decades to centuries. The C enters the atmosphere from different sources, both natural and anthropogenic. The major natural sources include (i) decomposition of OM and respiration by both plants and animals, (ii) volcanoes, (iii) natural brush and forest fires (iv) respiration by plants and animals, (v) CH_4 from the digestive system of wild ruminants and also from OM fermentation in wetlands, CH_4 from natural seeps and thawing of permafrost. The main anthropogenic sources include (i) CO_2 emissions from fossil fuel combustion in power plants and motorized transportation sector, CO_2 emission from cement production, steel mills and other industrial processes, (ii) CO_2 and CH_4 from agricultural soils—tillage, (iii) CH_4 from domestic ruminants, rice cultivation, (iv) land use change—conversion of forests and grasslands to arable land use.

In the terrestrial ecosystems, the C cycle exhibits natural cyclic behavior on range of timescales. Most ecosystems have a diurnal and seasonal cycle, which means that the ecosystem functions as a source of C in the winter and a sink for C in the summer, and this fluctuations is also detected in global annual atmospheric CO_2 concentration (Fig. 6.2). Large-scale fluctuations occur at other temporal scales as well, ranging from decades to centuries and longer (Harden et al. 1992; Braswell et al. 1997; Campbell et al. 2000; Min and Wu 2011). The global terrestrial ecosystem has been a net C sink over the last two and half decades (1990–2015), with a highly inter-annual variation, ranging from 0.3 to 5.0 Pg C yr^{-1} (Canadell et al. 2007a; Le Quéré et al. 2015, 2016). The interaction of climate with regional characteristics of ecosystems imposes complex climate controlling factors (e.g., temperature, precipitation, storm intensities, drought, and radiation) on carbon uptake in different vegetation and create local and regional climate regimes in the world (Braswell et al. 1997).

The net balance of C flows between atmosphere and the terrestrial biosphere also undergoes management-induced cycles that occur over long-time scales and that can cause the transition of terrestrial systems from sink to source and vice versa (Harden et al. 1992; Grosse et al. 2011). Human-induced changes that occur on an annual to centennial time scale are relevant for CO_2 sequestration and play significant role in climate change mitigation. These include the harvest cycle of managed production of forests. Mitigation options are intended to reduce atmospheric CO_2 relative to that which would occur without implementation of that option. The biological or ecological approaches to address increase in atmospheric CO_2 concentrations can be implemented in one of three strategies, namely: (i) conservation (i.e., conserving an existing C pools thereby preventing/minimizing CO_2 emissions to the atmosphere), (ii) sequestration (i.e., increasing the size of existing C pools by extracting CO_2 from the atmosphere by biological and/or ecological means), and (iii) substitution (i.e., substituting biological products for fossil fuel or energy intensive products thereby reducing CO_2 emissions).

Human activities have changed terrestrial C pools, with the largest changes occurring through the conversion of natural ecosystems to arable lands. It is estimated that such disruptions result in large reduction of vegetation biomass and loss of about 30% C in the surface 1 m of soil (Davidson and Ackerman 1993; Houghton 1995; Anderson 1995). It is estimated that globally, conversion of natural ecosystems to arable agriculture has resulted in losses ranging from 60 to 80 Pg C (Houghton 1995; Schimel 1995; Lal 2004), most of which occurring within few years to decades after land use conversion. In temperate zones, where there is little expansion of agriculture lands, currently losses of C have generally abated and the region has become a C sink (Janzen et al. 1998; Larionova et al. 1998; Le Quéré et al. 2015, 2016), while tropical areas remain an important source of CO_2 because of widespread clearing of natural vegetation, reduced fallow periods in shifting agriculture (Paustian et al. 1997; Scholes and vanBreemen 1997; Mosier 1998).

The general goal of human enhanced terrestrial C sequestration activities is to turn the global terrestrial ecosystems to C sink phase. If the system is disturbed (i.e., harvesting or burning of forests, land cultivation) large fraction of previously accumulated C may be released to the atmosphere, and when the ecosystem recovers from the disturbance it reenters a phase of active C accumulation. The disturbance history of terrestrial ecosystem involves large losses of C in the past (Houghton et al. 1999; Kurz and Apps 1999) and these become opportunities in C sequestration for the present. Increasing SOC stock may be achieved by growing plants that increase SOC storage in soils, or changing land use from arable to perennials, grassland or forest, introducing management practices that minimizes soil disturbance in arable land such as no-till (NT) or reduced tillage and cover crops following a system approach to conservation agriculture (Lal 2015). Although SOC sequestration does not continue indefinitely, the process is promoted as a means of slowing climate change by decreasing atmospheric CO_2 concentration while C-neutral and/or C-negative energy sources are developed.

The reservoirs of C inventory and C pools in each reservoir together with the exchange rate among different reservoirs are discussed in Chap. 6. Accelerated erosion decreases SOC by breaking up aggregates, increasing preferential removal of C in runoff or dust and increasing mineralization. The SOC of eroded soil may be reduced by as much as much as 70% compared to nearly 30% of non-eroded cultivated soil. Cultivated soil not prone to erosion generally achieve stable SOC within 30–50 years, organic soils when drained and cultivated are prone to decomposition and subsidence. Deforestation also leads to loss of SOC (Lal et al. 2003). If an area of unproductive or degraded land can be revegetated with permanent grass or trees, the land restoration leads to increase in stocks of OC, both in vegetation and soil, where C would otherwise have been in the atmosphere as CO_2. However, if the same strategy is applied on arable land used for food production, wider implications need to be considered. It is true that SOC stock is increased at the site of land use change (i.e., conversion of arable land to forest or grassland), but in most cases, some land is likely to be cleared elsewhere in the world to replace the lost food production. If the newly cleared land had native or semi-natural vegetation, and soils with high SOC content, then the loss of C at such sites will tend to counteract the sequestration from afforestation at the initial site. This effect is generally termed indirect land use change, and discussed mainly in the context of converting arable land to biofuel production (Searchinger et al. 2008), but is equally valid when considering the global impacts of afforestation or other approaches involving the removal of land from agriculture.

Soils used for arable land generally have a lower SOC content than the same soil type under natural or semi-natural vegetation. They are also subject to human management, therefore, the potential to increasing SOC stock and mitigating climate change is large. A range of management practices for increasing SOC stocks in arable land are discussed in Chap. 10. It is important to note that in many cases, the biophysical potential for increasing SOC stock cannot be realized because the required practices for achieving SOC sequestration potential under agriculture are less economic, less practical, and in some cases can conflict with the demands of food security.

9.2.2.1 Soil Carbon Sequestration and the Global Initiative

Building SOC content of soil under agriculture is not a novel enterprise, keen observers deduced since millennia the link between darkening SOC content and the fertility of the land, and preserving and replenishing SOC has remained an underlying aim of soil conservation for a long-term (Lal 2014). What is relatively new, however, is the realization within soil science community that the way we manage C in soil in agricultural fields has the implications beyond the agricultural fields, since C atom circulates unhindered within and among ecosystems traversing all arbitrary boundaries of space and time. Despite the realization of large SOC sequestration potential for the global cultivated agriculture lands among scientific community, soil C and the role of agriculture land in mitigating climate change was not on the agenda of the first 20 Conference of Parties (COP) to the United Nations Framework Convention on Climate Change (UNFCC) which started in 1995. However, the 21st conference (COP21) in Paris 2015 adopted the "4 per Thousand" initiative, a proposal calling for voluntary action plan to enhance SOC content of the top 40 cm depth of world soils at the rate of 0.4% yr^{-1}, and 50 countries, including U.S. have signed until 2016. Theoretically, soil under cropland could sequester 0.8–1.2 Mg ha^{-1} or about 88 Pg C over the next 50–75 years through implementation of this initiative (Lal 2016). This could be achieved through recommended management practices (RMPs) for enhancing C farming such as conservation agriculture, mulching cover cropping, biochar application, managed/improved grazing, restoration of degraded lands, agroforestry, and others. In addition to SOC sequestration, these practices also have ancillary benefits of improving food security. Other regional policy interventions include European Union's Common Agricultural Policy (CAP) which established Good Agricultural

Environmental Conditions (GAEC) requirement with the aim of reducing soil erosion, restoration of degraded lands and increasing SOC sequestration through RMPs (Panagos et al. 2016) which has been widely adopted in EU.

9.3 Conclusions

The global C cycle has been altered by the GHG emissions from the combustion of fossil fuels and by land use change and land use intensity. These perturbations have led to cumulative anthropogenic CO_2 emission of 600 ± 70 Pg C from the beginning of the industrial revolution in 1750 to 2015. Nearly 32% (190 ± 70 Pg C) of these emissions originate from land use and land use change, and for the recent decade, land use change was responsible for 10% of total anthropogenic C emissions. In addition, CH_4 and N_2O abundances in the atmosphere have increased by 154 and 21%, respectively over the same period. Agriculture plays significant role in emissions of CH_4 and N_2O. Achieving climate stabilization requires reduction of CO_2, CH_4, and N_2O, avoidance of GHG emissions and avoiding loss of sinks, and enhancement of the biological sinks of CO_2 to actively remove atmospheric CO_2. Avoidance of emissions is achieved through eliminating/minimizing deforestation and forest degradation, which is one of the largest opportunities available for mitigating climate change. Large deforestation emissions, especially in tropics illustrate the large mitigation potential associated with minimizing deforestation. The available biological activities that enhance C sequestration include afforestation and reforestation of abandoned agricultural lands, conservation and increasing soil C through management practices of agriculture lands, and bioenergy. The following chapters describe terrestrial C sequestration strategies in more detail.

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Chapter 10
Greenhouse Gas Mitigation under Agriculture and Livestock Landuse

Abstract Ensuring food security for the growing global population and changing climate are the principal challenges of the modern agriculture. The global population is projected to reach 9.7 billion by 2050. With rising incomes and the increasing proportion of global population living in urban areas, the composition of food demand is changing in fundamental ways. Higher income urban population have more diverse diets that feature a variety of high-value food sources such as livestock that are more resource-intensive to produce and process. This adds to the challenge of preserving the resilience of both natural resources and agricultural ecosystems. Agriculture occupies about 38% of the ice-free Earth's surface, of which, the cropland is about 12% and grazing land is about 26%. Projections indicate that global food production must increase by 70%, while in many African countries where the challenge is most acute, food production must increase by more than 100% by 2050 to meet the global food demand. The average annual share of agriculture, forest and land use to the total anthropogenic greenhouse gases (GHGs) has been declining over time from 28.7 ± 1.5% in the 1990s and 23.6 ± 2.1% in 2000s, and the annual value of 21.2 ± 1.5% in 2010. In 2010, agriculture contributed 11.2 ± 0.4% of the total anthropogenic GHG emissions compared to 10.0 ± 1.2% of the land use sector. Moreover, agriculture and land use changes associated with it are among the principal contributors of climate change. Agriculture also accounts for 84 and 52% of global nitrous oxide (N_2O) and methane (CH_4) emissions. Nonetheless, agriculture sector also is the most vulnerable to the adverse effects of global warming, such as more variable rainfall and more extreme weather generated events. Agriculture practices can potentially mitigate GHG emissions through improved cropland, animal husbandry, and grazing land management practices as well as restoration of degraded land and cultivated organic soils. Sustainable land management delivers benefits through C conservation in natural forests, grasslands, and wetlands, C sequestration in both agriculture soils and natural biomass, both of which remove C from the atmosphere and store it in biomass and soils within the terrestrial ecosystems. In addition, best management practices of croplands, grazing lands and also livestock and their byproducts such as manure could reduce the emissions of GHGs from agriculture and contribute to climate change mitigation.

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Contents

10.1 Introduction

The global agriculture is a dominant form of land management which covered 38% of the ice-free global terrestrial land surface in 2013. Croplands occupied 1408 million hectares (Mha, about 12% of Earth's ice-free land), while pastures occupied another 3521 Mha, about 26% of Earth's ice-free land in 2013 (FAOSTAT 2016; Foley et al. 2011), which supports 20 billion animals for grazing (Steinfeld et al. 2006). The global land area of 4929 Mha under agriculture in 2013 represents an increase of about 8% (363 Mha) since 1970, or about 0.2% per year (FAOSTAT 2016). An agroecosystem satisfies the basic needs of society of producing food, fiber, and bioenergy for the increasing population, but must do so sustainably, without undermining the global capacity to satisfy the future food, fiber and bioenergy production as well as other ecosystem services fundamental to human well-being (Foley et al. 2005, 2011; Rockstrom et al. 2009). Human economies and quality of life depend directly on the finite services and resources provided by the land. Agriculture, the dominant land use, is currently a significant environmental threat, being partly responsible for climate change, biodiversity loss, and degradation of land and freshwater quality (Power 2010). In addition to other environmental impacts, cropland management influences soil emissions of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). Anthropogenic GHGs emission from agriculture are much harder to quantify because agricultural GHG fluxes are complex and heterogeneous and it is not always possible to separate anthropogenic and natural GHG fluxes originating from land. The active management of agricultural production systems offers possibility for mitigation, and many of the agricultural mitigation opportunities can be implemented immediately.

Many of the stocks and flows within the global C cycle are reasonably well quantified and understood (Janzen 2004; Ciais et al. 2013; Le Quéré et al. 2015, 2016). There is a consensus that CO_2 emissions from land use and land use change are the second largest anthropogenic source of C into the atmosphere after fossil fuel combustion (Le Quéré et al. 2015, 2016), but these emissions are the most uncertain component of the global C cycle (Houghton et al. 2012), mainly due to comparatively limited global land use based emissions monitoring. The C emissions from land use change are a function of changes in C in the plant biomass and soils, the spatial distribution of C stocks, and the impacts of land management on biomass and soil C stocks. Land use and land cover changes are generally dominated by deforestation, i.e., conversion of forest to cropland, but also conversion of forests and natural grasslands to pastures and grazing land and also those of natural grasslands to cropland. Land use and land cover change releases significant amounts of CO_2 to the atmosphere. It is estimated that on average, deforestation has caused the loss of about 25% of soil organic C (SOC) over the years (Guo and Gifford 2002; Murty et al. 2002), largely due to oxidation of SOC as well as soil erosion. Crop and livestock production are the main causes of deforestation, especially in the tropics. After few years following land conversion, the net CO_2 emitted from cultivated land is generally considered neutral, mostly being associated to annual cycles of C fixation and oxidation through photosynthesis and respiration, however (Smith et al. 2007). The atmospheric increase in CO_2 concentration and that in nitrogen (N) deposition have resulted in a physical and biological response which has created natural terrestrial C sinks (Table 10.1).

Although CO_2 is the most abundant and important well-mixed GHG in the atmosphere, CH_4 and N_2O also contribute significantly to anthropogenic-induced climate change. Agriculture is the dominant source of anthropogenic N_2O and CH_4 emissions (Tubiello et al. 2015) and accounts for the largest share of non-CO_2 emissions (58% of global non-CO_2 emissions in 1990 and 54% in 2005), and although the sector's share is expected to decrease to 45% of global non-CO_2 emissions, it is expected to remain one of the largest contributor of emissions in 2030 (US-EPA 2012). Enteric fermentation and rice cultivation are the dominant sources of CH_4, and increasing use of N fertilizers is the dominant cause of anthropogenic N_2O emissions. The N_2O is generated by microbial transformation of N in soils and manures, and its emissions are enhanced where available N exceeds plant requirements, especially under wet conditions (Oenema et al. 2005). Emissions of both gases have increased by 1.6% annually from 1961 to 2010 (Tubiello et al. 2013). Agriculture is the second most important source of GHGs after fossil fuels uses, and together with land use change currently accounts for about a quarter of total anthropogenic GHGs emission. Therefore, in addition to ensuring food security under changing climate condition, the agricultural sector has a pivotal role to play in mitigating GHGs emission.

The net increase in agricultural land during 1980s and 1990s was more than 100 Mha across the tropics, and about 55% of the new agricultural land in the tropics

Table 10.1 Global annual fluxes of greenhouse gases in 2014–2015

Flux source	Mean annual flux (Pg yr^{-1})
CO_2 emissions (2014–2015)	
Fossil fuel combustion	9.9 ± 0.5
Land use change	1.3 ± 0.5
Total CO_2 emissions	11.2 ± 0.5
Atmospheric CO_2 growth	6.3 ± 0.2
Ocean sink	3.0 ± 0.5
Residual terrestrial sink	1.9 ± 0.9
Mean decadal CO_2 emissions (2006–2015)	
Fossil fuel combustion and cement production	9.3 ± 0.5
Land use change emissions	1.0 ± 0.5
Atmospheric growth rate	4.5 ± 0.1
Ocean sink	2.6 ± 0.5
Residual terrestrial sink	3.1 ± 0.5
Mean decadal CH_4 emissions (2002–2011)	
Fossil fuels	0.7 (0.6–0.8)
Agriculture	1.0 (0.9–1.0)
Other sources	0.8 (0.7–1.0)
Total emissions	2.5 (2.3–2.8)
Mean decadal N_2O emissions (2002–2011)	
Agriculture	0.5 (0.2–0.6)
Other sources	0.4 (0.1–1.3)
Total N_2O emissions	0.9 (0.3–1.4)

Data source Le Quéré et al. (2015, 2016), Canadell and Schulze (2014)

came at the expense of intact forests, while another 28% came from the conversion of degraded forests (Gibbs et al. 2010). The global cropland area land has decreased by 26 Mha since 2000, but in tropics, the agricultural land increased by 6 Mha mostly at the expense of forest loss (FAO 2016). On average, world agricultural production has grown by 2–6% yr^{-1} over the last 50 years, while the cultivated area has grown by 1% over the same period. Changing land use practices, technological advancement and improved varieties have enabled world grain harvest to double from 1200 to 2500 Tg yr^{-1} between 1970 and 2012 (FAOSTAT 2016). The rapid increase in food production in the second half of the 20th century has allowed supply and distribution to keep abreast with population growth and bring gains to food security for many regions. Average world cereal increased from 1.6 to 3.03 Mg ha^{-1} between 1970 and 2010 (FAOSTAT 2016). There was also more than 233% increase in fertilizer use from 32 Tg yr^{-1} in 1970 to 138 Tg yr^{-1} in 2013, and a 73% increase in irrigated crop land area (FAOSTAT 2016). Additionally, there has been a 1.4-fold increase in numbers of cattle, and buffaloes, sheep, and goats, which is closely linked with changing trends in CH_4 emissions in agricultural sector, and 1.6-fold increase in pigs and 3.7-fold increase in poultry from 1970 to

2010 (FAOSTAT 2016). Continuous growth has occurred in nearly all regions, but particularly pronounced growth occurred in Middle East, Africa and Asia.

Ensuring global food security in a context of growing population and changing climate is the principal challenge of the 21st century. The global population of 7.4 billion in 2016 is predicted to increase to more than 9.7 billion by 2050 (UN 2015). With rising incomes, and increased proportion of the global population living in urban areas are changing the demand and composition of food are changing in fundamental ways with significant increase in consumption of food of livestock origin. However, the last decade has seen a rapid reversal of the food production gains achieved in the second half of the 20th century. Achieving food security in the face of accelerating food demand, competition for depleting resources, and the failing ability of environment to buffer increasing anthropogenic impacts is now widely seen as the foremost challenge (Godfray et al. 2010; Ingram et al. 2010). Climate change is one of the interconnected risks facing agriculture and global food production systems (Pielke et al. 2007). Other global environmental challenges that are driving future food security include rapidly changing biodiversity, land cover change, availability of fresh water, and changing global nitrogen (N) and phosphorus (P) cycles. Increased climate variability is arguably one of the most consequential challenges for food security, particularly the livelihood of low-income communities with lower capacity for adaptation, with their food supply highly dependent on climate-sensitive activities such as rainfed agriculture and livestock production (Schmidhuber and Tubiello 2007). It is estimated that globally 25% of net terrestrial primary productivity (NPP) is appropriated by humans (Imhoff et al. 2004; Krausmann et al. 2013), and the global levels of appropriation will continue to increase as a result of population and economic growth and demand for bioenergy.

Agriculture, forest and land use change is responsible for about 25% of anthropogenic GHG emissions mainly from deforestation, emissions from livestock, soil disturbances and nutrient management (Smith et al. 2014). Similarly, the global GHG emission estimates from about 17 billion domestic food-producing animals vary from 8 to 18% of global anthropogenic GHG emissions (Gerber et al. 2013; US-EPA 2012; O'Mara 2011). The main sources of GHG include CH_4 from enteric fermentation and animal manure, N_2O from manure and slurry management and CO_2 from land use and land change (Gerber et al. 2013). Annual total non-CO_2 emissions from agriculture are estimated to be 0.2–5.8 Pg CO_2 equivalent yr^{-1} (Table 10.1; Tubiello et al. 2013; FAOSTAT 2016) comprising 10–12% of global anthropogenic GHG emissions. Agricultural non-CO_2 emissions increased by 0.9% yr^{-1} between 1990 and 2010 with slightly lower rate of increase after 2005 (Tubiello et al. 2013). Enteric fermentation and agricultural soils represent together 70% of total non-CO_2 emissions, followed by paddy rice cultivation, (9–11%) biomass burning (6–12%) and manure management (7–8%). Enteric fermentation is the major source of global agricultural GHG emissions, accounting for nearly 40% of global agricultural emissions, and over 70% of CH_4 emissions in 2014 (Fig. 10.1; FAOSTAT 2016; Yan et al. 2009).

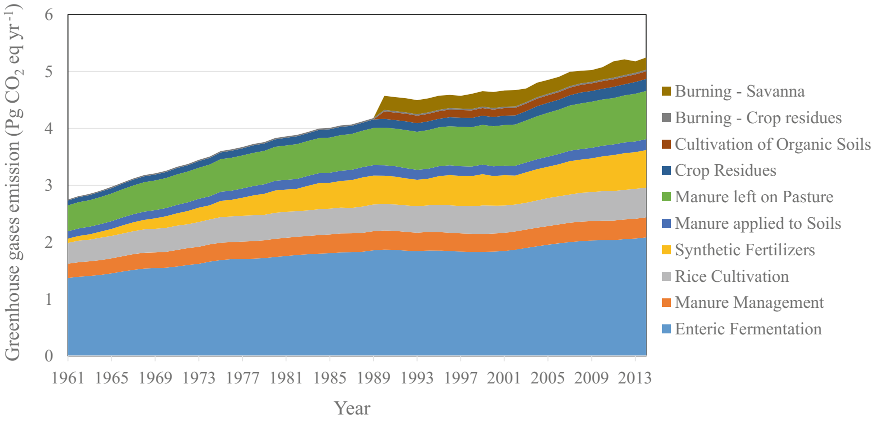

Fig. 10.1 Total annual greenhouse gas emissions from agriculture subsectors from 1961 to 2014. *Data source* FAOSTAT (2016)

As the global population continues to increase, demand for more diverse diet will also require additional resources for food production. Various projections suggest that global food requirements must increase by 70–100% by 2050 (Burney et al. 2010). Agriculture is highly vulnerable to climate change and needs to adapt to changing climate conditions. Even under optimistic lower end projections of temperature rise, climate change may reduce crop yields by 10–20% (Jones and Thornton 2009), while increased incidences of droughts and floods may lead to sharp increase in prices of some of the main food crops by 2050. Climate change will also impact agriculture through frequent incidences of pests and disease. As a result, the interaction between ecosystems and climate change are complex and their full implications in terms of productivity and food security remain uncertain (Gornall et al. 2010). Overall, increases in demand for food and bioenergy by 2050 may further increase pressure on forests in the tropics with a profound implication for increased GHG emissions.

Reducing emissions and enhancing resilience on climate change call for alternative approaches to practicing agriculture. Climate smart agriculture(CSA) seeks to increase productivity in a sustainable way, strengthening farmer's resilience and reducing agriculture's contribution to climate change by decreasing GHG emissions and increasing C storage (Campbell et al. 2014). Sustainable land management (SLM) involves practices that enable human being to maximize the economic and social benefits from land while maintaining or enhancing the ecosystem services from land resources. Sustainable management practices are alternative to conventional practices that lead to increased emission of GHGs from soils. Terrestrial C sequestration is the process which captures atmospheric CO_2 biologically through photosynthesis and store it as C in biomass and soils. It entails replenishing lost C and adding new C as organic inputs beyond the original levels. Historically, agriculture soils have lost 60–80 Pg C (Lal 2001) some of which can be recaptured through SLM practices. New technologies such as deep-rooted crops and pasture grasses can enhance original soil C up to a given equilibrium. The use of crop residues as mulch, intercropping, growing food crops with trees, and integrated nutrient and water management can also sequester C in agricultural soils. Soil C storage can also be increased by a variety of other practices including: (i) improved crop residue management, (ii) extended crop rotations, (iii) planting cover crops and perennial crops, (iv) soil erosion control, (v) improved water and nutrient management, and (vi) increased utilization of cultivation systems that require minimal tillage (i.e., reduced tillage, RT) or no tillage (NT) (Lal 2004c). These factors in one way or another alter the amounts of C entering the soil or its rate of decomposition. By adopting SLM practices to increase soil C, farmers can increase yields, reduce rural poverty, limit GHG emissions and reduce the impact of climate change on agricultural ecosystems. These practices favor C accumulation through multiple mechanisms.

The C storage on grazing lands can be increased by practices such as improved fire management and optimized intensity and timing of grazing. The objectives of this chapter are to describe the climate change mitigation options involving agriculture, the processes and technological options of C sequestration in terrestrial C pools so as to reduce the net rate of increase of atmospheric concentration of CO_2 with specific attention to agriculture and grassland soils. In this chapter, the comprehensive synthesis of knowledge on the impact of different land management practices on soil C sequestration rates will be evaluated.

10.2 Carbon Sequestration

The global C cycle consists of two major components differing in timescales of cycling: (1) geological cycle that acts over epochs but cycles large amount of C because of longer time period and spatial scale involved, and (2) a biological cycle that operate at a much shorter period of time (Chap. 5). In addition to perturbation of the biological C cycle, the anthropogenic activities during the industrial period have released geological C at a much faster rate than its natural cycling rate, resulting into ongoing problem of climate change. At the same time, we are attempting to fix the problem of increase in atmospheric CO_2 that stems from the exploitation of geological C cycle the manipulation of the biological C cycle. Because the two cycles operate at two different timescales, there is a large amount of C to exploit from geological reserves, but little capacity to fix this large geological C within the biological cycle. However, it is worth noting that the two cycles are not entirely distinct, since soil C cycle and chemical C cycling sits somewhat in between the two, and annual biological cycling of plants is capable of long-term physicochemical preservation of C in soils for thousands of years if some interventions in the short-term natural cycle are balanced in favor of increased net input or storage of C in soils through (i) increasing the rate of OM input to soils, (ii) reducing the rate of its decomposition by biological, physical or chemical means, (iii) increasing the rate of its stabilization through physico-chemical and biological protection, and (iv) increasing the total volume of soil sequestering the C at a maximum rate by transferring C to deeper depths (Whitmore et al. 2015).

The CO_2 emission rates from fossil fuel combustion and cement production between 1990 and 2014 increased by 53% (Le Quéré et al. 2015). However, the amount of CO_2 accumulation in the atmosphere over the same period increased by 26%, nearly half of the anthropogenic CO_2 emissions, suggesting that the global mean atmospheric CO_2 growth is substantially lower compared to emissions. This is because some of the excess CO_2 released is removed by oceans, forests, soil and other ecosystems. Considering decadal anthropogenic CO_2 emissions of 6.3.0 ± 0.5, 8.0 ± 0.5, and 9.3 ± 0.5 Pg C yr^{-1} for 1990–1999, 2000–2009, and 2006–2015, respectively (Le Quéré et al. 2015, 2016), it implies the existence of large global terrestrial C sinks (Pacala et al. 2001; Sitch et al. 2015). Le Quéré et al. (2015, 2016) estimated global residual terrestrial C sink of 2.3 ± 0.5 and 2.6 ± 0.5 Pg C yr^{-1} for the decades of 2000 to 2009 and 2006 to 2015, respectively. This process of transferring atmospheric CO_2 into long-lived C pools that would otherwise accumulate in the atmosphere is termed C sequestration, which can be a natural or anthropogenically driven process (Lal 2008). The overall objective of anthropogenically driven C sequestration process is to balance the global C budget such that future economic growth is based on a carbon-neutral or carbon-negative strategy, either with no net gain or net-removal of atmospheric C pools. To achieve C neutral strategy, it will require sequestering generated CO_2 through safe, environmentally acceptable and stable techniques with low risk of leakage to the atmosphere. The options for C sequestration can be grouped into two broad categories namely: (1) abiotic C sequestration, and (2) biotic C sequestration. The abiotic C sequestration is based on physical, chemical and geoengineering techniques that removes of CO_2 from the atmosphere, which does not involve intervention of living organisms. These techniques are explained elsewhere in this volume. The biotic sequestration is based on managed intervention of higher plants and microorganisms in removing CO_2 from the atmosphere. In this chapter, biological sequestration options involving agricultural activities are discussed. The options involving forest management are discussed in Chap. 11.

10.2.1 Organic Carbon Sequestration in Plant Biomass and Soils

Soil C sequestration is generally defined as any increase in the soil C content resulting from a change in management within the same landscape such that additional C is held onto soil and is separated from the other parts of ecosystem (Lal 2008; Powlson et al. 2011). It occurs when a positive disequilibrium is sustained over some period of time, with the soil system eventually achieving a new, higher steady-state of C stocks, generally by withdrawing C from atmospheric CO_2. In addition to mitigating the climate change, increase in SOC has numerous ancillary benefits—such as improved soil and water quality, restoration of degraded ecosystems, and increased crop yields. C sequestration contributes to climate change mitigation if the change in management practices causes a net additional transfer of C from the atmospheric CO_2 to the terrestrial biosphere—such as soil or vegetation, thus slowing or even reversing the increase in atmospheric CO_2 concentration. This could be achieved by increasing the net photosynthesis and/or slowing the rate of SOC decomposition through change in land management—such as reduced intensity of tillage or altered management. Because storage of SOC is dynamic, i.e., C derived from the atmosphere is ultimately recycled back to the atmosphere, the residence time of C in soil is a major determinant of the capacity of soil to sequester C (Luo et al. 2003). However, not all practices that increase SOC content represent a transfer of additional C from atmosphere to the land, since some practices move C from one pool within biosphere to another without affecting the atmospheric CO_2 concentration and therefore with no implications for climate change. Powlson et al. (2011) proposed that the term ‘C sequestration’ to be used only for the situations where there is an additional transfer of C from the atmosphere and genuine contribution to climate change mitigation.

Food systems contribute significantly to the global warming and are responsible for 19–29% of global GHG emissions, the bulk of which comes directly from agricultural production activities—i.e., N_2O and CH_4, and CO_2 coming indirectly from land cover change driven by agriculture (Vermeulen et al. 2012). Soil C sequestration connotes both an increasing the amount of C stored in soils as well as maintenance of C stocks over an extended period to balance the global C budget, such that future economic growth is based on C neutral strategy with no net gain in atmospheric C pool (Lal 2008). A combination of biological, chemical, and physical processes results in soil storage of about three times (to 1 m depth) as large as living vegetation. Different ecosystem types store different amount of C depending on species composition, soil type, climate, relief, and other biophysical features. Of the estimated 150 million km^2 of the terrestrial ecosystems area, forests accounts for about 28%, savannahs and grasslands both cover about 23%, while croplands occupy about 11% (Table 10.1). As described in Chap. 6, global C cycle transfers C in Earth’s atmosphere, vegetation, soils, and oceans. The two most important anthropogenic processes responsible for the release of CO_2 into the atmosphere are fossil fuel burning and land use change. Current land use change emissions are 1.6 ± 0.5, 1.0 ± 0.1, and 1.0 ± 0.8 Pg C yr^{-1} for 1990–1999, 2000–2009, and 2006–2015 decades, respectively, and about 1.3 ± 0.5 Pg C yr^{-1} in 2015 (Le Quéré et al. 2015, 2016), largely determined by tropical deforestation that exacerbates SOM decomposition and soil erosion. Tropical deforestation is mainly fueled by population growth and the attendant demand for natural resources, urban expansion, poverty, and international trade.

Soils affect the C cycling and dynamics via being the link between the atmosphere, vegetation and oceans. Globally, the pedologic pool of C is estimated at 2500 Pg C up to 1 m deep, of which inorganic C is estimated at 950 Pg C (Batjes 1996). A combination of biological, chemical and physical processes results in soil C storage. Global soils (up to 1 m depth) store about three as much C as vegetation, and more than three times the size of atmospheric C pool. The term soil C sequestration, as used in this chapter, generally connotes an increase in amount of C stored in soil and also maintenance of C stocks over the extended period of time, thus slowing or even reversing the increase in atmospheric concentration of CO_2. Increased storage of SOC occurs via increased C inputs, reduced C losses, or both. The C lost through decomposition returns CO_2 to the atmosphere, but local losses due erosion and subsurface transport to groundwater lead to C redistribution over the landscape (Jardine et al. 2006; Izaurralde et al. 2007; Van Oost et al. 2007), but cannot be considered as sequestration and may lead to increase in emission (Lal 2003).

Different fractions of SOC pools have different functions within the soil system. Crop residues are readily mineralized and serve as substrates to soil microorganisms. Particulate OC (POC) is mineralized relatively quickly but slower than that of other crop residues, and is important for soil structure, energy for biological processes, and provision of nutrients for plants. A more stable C fraction can be classified into active or recalcitrant C. Recalcitrant OC is highly stable, insoluble form that is not subject to further decomposition, and is important for soil physical structure, water retention, and tilth, while active fraction (i.e., active humus) is an excellent source of plant nutrients. Some very stable recalcitrant OC complexes can remain in the soil for centuries to millennia. Physical protection of SOC against the microbial processes is an important mechanism to increase the mean residence time (MRT) (Dungait et al. 2012). The C residence time is the key factor affecting sequestration potential in different soils (Luo et al. 2003). Even with constant input, conditions or manipulations that increase MRT lead to enhanced sequestration. When the primary control on MRT is limited, decomposition caused by environmental extremes (e.g., low temperature, low O_2, C inputs) may be sequestered without any constraint (i.e., boreal peat deposits). The sequestered C is vulnerable to release from storage if environmental conditions that moderate its storage are changed (Freeman et al. 2001). Under more biologically favorable environmental conditions, biogeochemical transformation and physicochemical protection (Dungait et al. 2012) are the primary mechanisms controlling SOC MRT (Jastrow et al. 2007).

At a global level, the SOC pool is concentrated in five major soil orders: Histosols, Inceptisols, Entisols, Alfisols, and Oxisols (Table 10.2). In the tropics, the largest amount of SOC is found in Oxisols Histosols, Ultisols and Inceptisols. Overall, the SOC pool represents a dynamic balance between gains and losses. The amount changes over time depending on photosynthetic C inputs added and the rate of its decomposition. Under undisturbed natural conditions, inputs of SOC from litter fall and root biomass are cycled with output through erosion, OM decomposition, and DOC leaching. The potential C sequestration is controlled primarily by pedological factors set by physicochemical maximum limit to storage of C in soils—including soil texture, clay mineralogy, soil depth, bulk density, aeration, and proportion of coarse fragments. Net primary productivity (NPP) is the main factor influencing the attainable sequestration, and is modified by aboveground versus belowground allocation. Land management practices that increase C input through increasing NPP tend to increase the attainable level to near the potential level. Climate has both direct and indirect effects on attainable sequestration, since

Table 10.2 Global biomes and C stock in vegetation and top 1 m soil of the world biomes

Biome	Area (million km^2)	Carbon stocks (Pg C) in the ecosystem		
		Vegetation	Soils	Total
Tundra	9.5	6	121	127
Boreal forests	13.7	88	471	559
Temperate forests	10.4	59	100	159
Tropical forests	17.6	212	216	428
Temperate grasslands	12.5	9	295	304
Tropical savannahs	22.5	66	264	330
Wetlands	3.5	15	225	240
Deserts	45.5	8	191	199
Croplands	16	3	128	131
Total	151.2	466	2011	2477
Proportion (%)		19	81	100

Adopted from Watson et al. (2000), Ravindranath and Ostwald (2008)

the decomposition rate increases with increase in temperature, but decreases with increasing anaerobic conditions. Theoretically, the potential SOC sequestration capacity is equivalent to cumulative historical C loss. However, only 50–66% of this capacity is attainable through the adoption of sustainable land management practices (Lal 2004a).

10.2.2 Inorganic C Sequestration in Soils

Soil C sequestration may also involve soil inorganic C (SIC), although SOC sequestration has been studied more than SIC, because SIC sequestration is restricted to sparsely populated arid and semiarid climate. The exchange of SIC (i.e., various soil carbonate minerals, mostly calcite with the atmosphere) is much slower, and viewed as unresponsive to land management, with MRT of ~78,000 years and viewed as non-responsive to management (Schlesinger 1985). Nevertheless, the global SIC pool is recognized to be large—940 Pg C (Batjes 1996), exceeded only by the amount of C in ocean (~38,000 Pg C) and SOC (~1505 Pg C) (Sarmiento and Gruber 2002; Batjes 1996), reflecting the importance of SIC globally in long-term. It is widely recognized that unlike SOC, SIC concentrations in soil is not controlled by vegetation community, but it can accumulate to highly concentrated levels such as those in petrocalcic horizons. Large stocks of SIC are mostly found in regions with low water availability (i.e., arid, semi-arid, and sub-humid regions (Eswaran et al. 2000). Low precipitation and high evapotranspiration strongly limit the dissolution and leaching of carbonates from soil. Based on origin, formation and morphology, the SIC can be sub-divided into three groups: (1) geogenic carbonates—carbonates that remained or are inherited from soil parent materials such as limestone particles or carbonates allocated onto soil from other locations by calcareous dust or landslides, (2) biogenic carbonates—carbonates formed within terrestrial animals and plants as part of their skeleton, such as bones, shells, calcified seeds, or released by certain organisms such as esophagus of earthworms, and (3) pedogenic carbonates—carbonates formed and redistributed in soils through dissolution of SIC pool (i.e., geogenic, biogenic, or previously formed pedogenic carbonates) (Zamanian et al. 2016).

Secondary carbonates are formed in soils at pH 7.3–8.5 in the presence of sufficient Ca^{2+} and/or Mg^{2+} in the soils. Decreasing water content, decreasing partial pressure of CO_2 or HCO_3^- favor precipitation of secondary carbonates. Inorganic C can be sequestered in soils (Martens et al. 2005), but the rates of sequestration are low (VanDam et al. 1997; Monger et al. 2015). The formation and accumulation of carbonate minerals in soils can directly mitigate increase of atmospheric CO_2 (Xie et al. 2009), if Ca^{2+} have been released to the soil from sources other than CO_3^{2-} containing minerals such as weathering of igneous rocks, decomposition of OM or dissolved Ca^{2+} in rain water (Monger et al. 2015). SIC is comprised of soil carbonates and bicarbonates, which account for $\sim$940 Pg C as carbonates in soils and $\sim$1404 Pg C as bicarbonates in groundwater (Monger et al. 2015). The proposed mechanisms and processes controlling the sequestration of inorganic C in both soil carbonates and groundwater is through weathering of silicate minerals (Monger et al. 2015). The inorganic forms of soil C, primarily resulting from mineral weathering are less responsive to land management.

Overall, the role of SIC as a method for C sequestration is viewed as less significant (Schlesinger 2000) due to three main reasons: (1) in order for soil carbonates to sequester atmospheric CO_2, carbonate source must come from silicate minerals and not from the pre-existing carbonates, and distinguishing Ca^{2+} originating from silicate minerals from a carbonate source is difficult, (2) carbonate accumulation occurs at a much slower rates, at timescales of thousands of years (Monger and Galleros 2000; Monger et al. 2015), (3) quantifying sequestration by soil carbonate is also difficult because many soils contain both pedogenic carbonate and lithogenic carbonate, which cannot be differentiated using routine measurements of $CaCO_3$ equivalents. However, progress has been made to track the source of Ca^{2+} by using strontium (Sr) isotopes as a proxy indicator (Capo and Chadwick 1999; Naiman et al. 2000), and also using C isotopes and micromorphology techniques (Nordt et al. 1998; Kraimer and Monger 2009).

10.3 Nature of Soil Organic Carbon Inputs and the Mechanisms for Its Stabilization in Soils

Terrestrial C pool assimilate an estimate of 123 ± 1.2 Pg C yr^{-1} from the atmosphere in the form of gross primary productivity (GPP) as photosynthesis (Ciais et al. 2013). Some of C is returned to the atmosphere through plant respiration and biomass fires, and some is retained by the terrestrial ecosystems as plant biomass. The amount of C stored in soil represents one of the largest reservoirs of SOC on a global scale. Consequently, any changes in the size and turnover rate of soil C pools may potentially alter atmospheric CO_2 concentration and the global climate. The CO_2 flux from the soil to the atmosphere (i.e., soil respiration) is the second largest terrestrial C flux in the global C cycle, and is primarily made of autotrophic respiration consisting of root respiration and heterotrophic respiration (i.e., soil organic matter decomposition) (Bond-Lamberty and Thomson 2010a), and it is estimated to range from 75 to 100 Pg C yr^{-1} (Raich and Potter 1995; Hashimoto et al. 2015). Soil respiration is the main contributor to ecosystem respiration (Malhi et al. 1999) and therefore, plays a role in determining the carbon balance of terrestrial ecosystems. The ecosystem respiration is about 60 times the annual contribution of land use change, and an order of magnitude larger than fossil fuel combustion (Le Quéré et al. 2015), implying that $\sim 10\%$ of the atmospheric CO_2 cycles through the soil annually (Reichstein and Beer 2008). Therefore, a small change in soil respiration can significantly alter the balance of atmospheric CO_2 concentration and cause significant impact on SOC storage.

Soil respiration is sensitive to environmental factors e.g., temperature and precipitation, (Hashimoto et al. 2011), and is regulated by several factors including soil moisture, vegetation type, N content, and level of aeration in the soil. Future climate change is expected to increase the rate of soil respiration at the global scale (Bond-Lamberty and Thomson 2010b). Higher temperatures trigger microbes to speed up their consumption of plant residues and other organic matter. Variations in temperature are significantly and positively correlated with changes in global soil respiration (Bond-Lamberty and Thomson 2010b). Soil respiration increased by 0.1 Pg yr^{-1} between 1989 and 2008, and reached roughly about 98 Pg yr^{-1} in 2008, about 10 times more C than anthropogenic release into atmosphere each year. It is estimated that a rise in temperature by 2 °C will release additional 10 Pg C yr^{-1} to the atmosphere through soil respiration (Friedlingstein et al. 2003).

Tillage operations can significantly affect soil respiration. Conventional tillage (CT) leads to the destruction of soil aggregates, excessive respiration, and SOM decomposition, leading to reduced crop production, and decreased resilience of the ecosystem (Lal 2015). In addition, excessive application of N fertilizer can markedly increase root biomass and stimulate soil respiration rates. When other factors are at optimum, conservation tillage, use of cover crops, such as green manure, crop rotations, use of deep-rooted crops, application of manure, and water management can optimize soil respiration in addition to increasing SOC input. For agriculture crops such as cereals and forage plants, the existing data indicate that during growth of plants to maturity, about 20% (for cereals) to 50% (for forage) of the total assimilated C that is translocated to the roots is subject to decomposition (Kuzyakov et al. 1999; Kuzyakov and Domanski 2000). Root cell-wall debris containing lignin and suberin is often regarded as the precursor to stable OC (Rumpel et al. 2002). Root-derived hydroxyl alkanoic acids originating from cutin and suberin are preferentially preserved compared with phenols originating from root-derived lignin in acid subsoils and contribute to SOC in mineral subsoils

(Rumpel et al. 2002; Nierop and Verstraten 2003; Nierop et al. 2003). At molecular level, properties that influence the decomposition rates of natural substances are molecule size, polarity, ether-bridges, quaternary C atoms, substituted N-linkages, phenyl and heterocyclic N-groups, and long-chain hydrophobic hydrocarbons (von Lützow et al. 2006).

Decomposition of SOM plays an essential role in terrestrial C cycling (Knoblauch et al. 2013), since it facilitates the growth and life of soil biota by providing energy from C compounds and nutrients in inorganic forms for the soil biota. Considerable efforts have been aimed at understanding the mechanisms responsible for variability in decomposition rates of SOM among soil types, OM types, and different climatic conditions e.g., (Craine et al. 2010; Xu et al. 2016). Despite these efforts, it is still not satisfactorily known how SOC decomposition rates vary at a large spatial scale and which factors control SOC decomposition. The requirement for accurate accounting of spatial and temporal variability of SOC decomposition is central to better prediction of the amount of SOC sequestered and processes responsible for SOC retention and release in different soils. The SOC consists of a continuum of OC components ranging from labile compounds that mineralize rapidly during the first stage of mineralization to highly recalcitrant residues that accumulate at the advance stages of decomposition either through selective preservation or microbial re-synthesis (Elberling et al. 2013). For the purposes of modeling soil S dynamics, the SOC pool is conceptualized to contain at least three identifiable C pools with different MRT: (i) the active, (ii) the intermediate (slow), and (iii) passive (recalcitrant) C pools (Trumbore 1997; Luo et al. 2003). These pools are generally differentiated based on the MRT of SOC, which is extremely variable, ranging from a few days to several centuries or even millennia (Trumbore 1997). The mechanisms through which soil organic compounds persist in soil are not fully understood, but are believed to include a variety of biological, physical, and chemical processes (Sollins et al. 1996; Schmidt et al. 2011). The differences in MRT reflect a combination of the intrinsic decomposability of the OM and the constraints on decomposition, and suggest that C stability in the soil depends on its biotic and abiotic environment, while the molecular structure of plant inputs and OM could play secondary role in determining MRT ranging from decades to millennia (Schmidt et al. 2011). For example, OM in subsoil horizon is characterized by turnover times that increases with depth—with radiocarbon ages of 1000 to >10,000 years (Schmidt et al. 2011). Accumulation of C in deep soil may occur because of combination of factors including (i) scarcity of microbial substrates such as labile organic compounds, available nutrients, or molecular O_2 that limit microbial activity or enzyme production (Kuzyakov 2010), (ii) environmental conditions such as low temperature or low pH (Hagerty et al. 2014; Mobley et al. 2015), (iii) inaccessibility and physical protection in soil matrix, either occluded or bound by clays (Six et al. 2002; Schmidt et al. 2011), and (iv) chemically low degradability of accumulating organic compounds conferred by their nature or low N content (Sollins et al. 1996; Hernes et al. 2007). Additionally, root-derived C is generally retailed in soils much more efficiently that the above-ground C inputs of leaves and plant needles (Rasse et al. 2005; Kong and Six 2010). Furthermore, physical disconnection between the decomposers and SOM play important role in SOC stabilization in soil, and is likely one of the reason for the persistence of deep SOC (Chabbi et al. 2009).

Soil C in various stages of alterations can be protected by an array of molecular associations with mineral surfaces, and various mechanisms can be involved in the interactions of OC with mineral surfaces, including ligand exchange, polyvalent cation bridges, and other weak interactions such as hydrophobic interactions, Van der Waals forces and H-bonding (Kaiser and Guggenberger 2000). These largely chemical interactions depend on various factors, including the characteristics of the organic matter, reactivity and specific surface of soil minerals, base-cation status, presence of Fe and Al oxides, pH, and redox conditions (von Lützow et al. 2006; Lehmann and Kleber 2015; Doetterl et al. 2015). Therefore, in addition to climatic factors, SOC stabilization is controlled by the geochemistry of soils and effects of soil mineralogy, and these plays crucial role in SOC turnover in many soils.

There are a range of factors that regulate C decomposition in soil as (a) climatic factors e.g., temperature, water content (Wang et al. 2013), (b) soil properties, e.g., clay and silt content, water holding capacity, C:N ratio, specific surface area (Xu et al. 2016), (c) geographical variables e.g., latitude and longitude (Wang et al. 2013), (d) biological composition of SOC, and soil microorganisms (Morales and Holben 2011). In general, SOC inputs are biologically altered to forms that are relatively more resistant to decomposition (i.e., selective preservation) and long turnover times, and in some cases, are stabilized by sorption on mineral surfaces (Kögel-Knabner 2002; von Lützow et al. 2006) and/or spatial inaccessibility (von Lützow et al. 2006). Sollins et al. (1996) proposed three major mechanisms that protects SOC form decomposition in soil as: (i) molecular characteristics of OM, i.e., recalcitrance, (ii) low accessibility for biological degradation, and (iii) interaction with mineral particles. In contrast, biological stabilization scheme based on three mechanisms namely biological recalcitrance, biological capability of the decomposer community, and physical protection has been proposed (Baldock et al. 2004). Conceptual model suggests that the biologically recalcitrant chemical structures are alkyl C and charred OM, while other mechanisms are responsible for the protection of potentially labile molecules of SOC, leading to variable chemical structures observed for the stored SOC (Baldock et al. 2004). Accumulation of SOC is a result of positive imbalance between inputs and outputs from SOM, and C accrual can be driven by an increase in photosynthetically derived C inputs, decrease in C losses, or both. Leaching, runoff, and erosion can contribute to C losses from any given location, but have a potential to add C input elsewhere. Protection of biochemically altered SOC from further microbial decomposition or extracellular enzyme is essential to lengthen the MRT of C in soils. The physicochemical protection of SOC is affected by numerous processes, including diffusion of soluble or colloidal C, advection of dispersed particles, mechanical actions of plant and fungal growth, mixing by soil fauna, localized hydration changes, freeze–thaw cycles, and mechanical disturbances, such as tillage (Six et al. 2004; Jastrow et al. 2007). Potentially greater protection occurs when microbial access to substrates is physically impeded or when soil structural controls on gas exchange and moisture conditions inhibit decomposer activity (Young and Ritz 2000).

In general, clay content is assumed to be positively correlated with preservation of SOC (Xu et al. 2016). Decomposition of SOC is generally lower in soils with high clay concentrations (Balesdent et al. 2000) because soil minerals can protect SOC from enzymatic attack, and chemically the strength of the interaction of the chemical structure of SOC with minerals and organic soil component defines the degree of protection of SOC (Six et al. 2002). In general, SOC in fine silt and clay is older or has a longer turnover time (Balesdent 1996; Eusterhues et al. 2003; Thaymuang et al. 2013). For tropical and subtropical soils, the higher stability of OM in clay separates is related to the presence of variable charge minerals, particularly kaolinite, iron, aluminum oxides and allophane (Bayer et al. 2006). Biochemical alteration of SOC is inhibited, and residence time is significantly increased by interactions of SOC with soil minerals. A detailed mechanistic understanding of how sorption to soil minerals reduces OC mineralization is limited by artefacts in the experiments, however. The adsorption of macromolecules is generally considered non-reversible and associated with conformational changes that render macromolecules unavailable to the action of extracellular enzyme (von Lützow et al. 2006).

Plant and mycorrhizal litter is fragmented into particulate organic matter, which is then further decomposed. Throughout this process, C assimilated by soil biota and used for growth is similarly transformed after these organisms die, and their wastes and extracellular products are decomposed. New, larger polymers are then assembled from the smaller molecules released during decomposition. The resulting compounds, historically and collectively known as humus, do not have well-defined composition or structure, but increasing evidence suggests they may consist of dynamic clusters of chemically altered and unaltered compounds held together loosely by hydrophobic interactions and hydrogen bonding (Piccolo 2002; Sutton and Sposito 2005). Hydrophobicity reduces surface wettability, and thus the accessibility of OC for microorganisms, which results in reduced decomposition rates, since the absence of water restricts the living conditions of microbes and also inhibits the activity of hydrolyzing enzymes (von Lützow et al. 2006).

Soil enzymes play essential role in decomposition and mineralization of SOC in soils, and their activities are key drivers of nutrient supply to plants. Extracellular enzymes are key biological indicators of soil quality, because they are sensitive to environmental stress and respond rapidly to changes in land management. Many SOC transformations in soils are caused by extracellular enzymes excreted by microorganisms. Enzyme production, activity, and longevity depend on the proximity of substrates, the number of sorption sites on substrates, and enzyme sorption affinities for soil minerals (Schimel and Weintraub 2003; George et al. 2005). Soil enzyme activities are generally regarded as sensors of SOC decomposition because they integrate the information about microbial status and soil physical-chemical properties (Sinsabaugh et al. 2008).

Soil pH, redox conditions, and mineralogy are additional factors affecting the reactions (Jastrow et al. 2007). Many soils also contain significant amounts of pyrogenic C from periodic burning in situ or atmospheric deposition from natural fires and industrial sources (Schmidt and Noack 2000). Collectively known as black C, these highly condensed aromatic compounds, also termed as charred OC that represent a continuum from partly charred material to graphite and soot particles. Black C contributes up to 45% of SOC in Chernozemic soils in Germany (Brodowski et al. 2005) and as high as 80% of SOC in highly industrialized areas of Germany as a result of combusted coal particles and coal dust from coal processing industries (Rumpel et al. 1998). Charred C is also found in sediments and water bodies, and can comprise up to 40% of total SOM in grasslands and boreal forests (Preston and Schmidt 2006). On a relative scale, most black C forms are more recalcitrant than biogenic C in soil, and MRT can be hundreds to thousands of years (Glaser et al. 2002; Laird et al. 2008). However, there is a lack of data on the turnover times or the age of charred OC in soils, and therefore, a true recalcitrance of charred OC in soils has still to be shown. It suffices to say that pyrogenic soil C is by no means inert, and under certain conditions, some forms can be readily oxidized or biochemically degraded (Bird et al. 1999; Hamer et al. 2004), but its decomposition pathways are not well known. The optimization and standardization of the determination of charred OC is still a field for future research to establish the potential for charred OC as one of the solutions for increasing concentrations of CO_2 in the atmosphere and its potential role for climate change.

Physical protection of C is intimately tied to processes responsible for creation, turnover, and stabilization of soil aggregates at multiple, often hierarchical, scales (Six et al. 2004). Although minimal long-term protection of SOC is afforded by macroaggregates (>250 μm in diameter), their formation slows the mineralization of fresh C inputs, and their turnover rates control the longer-term stabilization of C within microggregates (50–250 μm) (Six et al. 2004). Even greater increases in MRT of C result from occlusion of C in silt- and clay-sized aggregates, which likely form within microaggregates (Balabane and Plante 2004). Aggregate structure and dynamics also influence soil porosity, which controls the distribution and activity of decomposers and their enzymes (Young and Ritz 2000; Ekschmitt et al. 2005). Substrates inside pores with necks can lead to anaerobic spaces within largely aerated aggregates and to localized limitations on decomposer activity (Young and Ritz 2000).

The various stabilization mechanisms operate at different time scales (von Lützow et al. 2006), and their interactions lead to a continuum of SOC pools with MRTs that can range from < a year to centuries and even millennia. Further, the effectiveness and relative importance of different mechanisms vary with soil type and other conditions, and current evidence indicates that most stabilization mechanisms can become saturated (Six et al. 2002). While the unique physical and chemical properties of a given soil may define an overall saturation limit (i.e., additional inputs will not lead to additional sequestration), management methods and environmental conditions likely determine a lower "effective saturation capacity" (Stewart et al. 2007). The duration and efficiency of sequestration for a given soil are therefore related to its saturation deficit, that is, the difference between initial C stocks and those at its effective saturation capacity (West and Six 2007).

In general, persistence of SOC in soils involve complex interactions between organic matter and environment, including compound chemistry, reactive mineral surfaces, climate, water availability, soil acidity, soil redox state, and the presence of potential degraders in the immediate microenvironment. The nature and chemistry of SOC could be important for the decomposition rate, but its influence on the decomposition depends on other environmental factors. Based on these factors, OC can therefore, be described by the quantifiable environmental characteristics governing stabilization such as solubility, molecular size, and functional groups (Kleber 2010). Therefore, improved understanding of SOC destabilization is needed to enhance the efforts to avoid soil degradation and accelerate recovery of the degraded soils.

10.4 Greenhouse Gases Emission Trends from Agriculture

Agriculture is the source of human food, animal feed, fiber, and fuel and also play the key role in efforts to achieve global sustainable development. Transformation of natural ecosystems into managed land for agricultural use has accelerated since 1950, coinciding with the global population growth from 2.5 billion to an estimated 7.4 billion in 2016 (UN 2015). As a result, almost all soils are subject to some degree of human disturbance, either directly through land use and land management or global change such as pollution and climate change, and more than half of Earth’s land surface is intensively used for agricultural purposes, such as cultivation, grazing, plantation forestry, and aquaculture. It is estimated that since 1950, about one third of the soils have been altered from their natural ecosystem state because of moderate to severe soil degradation (Oldeman 1998). However, distinguishing natural from direct or indirect anthropogenic influence and the associated natural and anthropogenic GHG emission is not always straight-forward (Smith 2005), but some anthropogenic activities and the related consequences have clear impacts. Impacts on soils largely emerge from the need to meet the food, fiber, and fuel demands for a growing population including an increase in meat and other animal sourced consumption as the developing nations becomes wealthier and increasingly more urbanized. Additionally, demands for bioenergy adds pressure to the land resources. These changes have led to conversion of natural land to managed land—i.e., extensification as well as intensification as agriculture and other management practices on existing land such as increased nutrients and water and increasing harvest frequency to increase yield per hectare. Land use change such as conversion of forest or natural grassland to pasture or cropland removes biomass, change vegetation and disturbs soil leading to loss of soil C and other nutrients, changes in soil properties and change to above- and below-ground biodiversity.

The environmental impacts of agriculture includes those caused by expansion i.e., when croplands and pastures extend to new areas, replacing natural ecosystems, and those caused by intensification i.e., when existing lands are managed to be more productive through fertilizers, irrigation, pesticides and mechanization. Agriculture expansion has had a significant impacts on habitats, biodiversity, C storage and soil conditions (MEA 2005). Land cover change has been dominated by deforestation, but also conversion of grassland to cropland and grazing land. Deforestation has had the greatest impact on average around 25% of soil C could be lost (Guo and Gifford 2002; Murty et al. 2002). Soil losses stem from oxidation of OM and soil erosion. Inorganic and organic materials provided as inputs to agriculture as well as organic biomass output from agricultural systems are typically broken down by microbial processes and release significant amounts of CO_2, CH_4, and N_2O to the atmosphere. However, except where natural vegetations are cleared, nearly all of CO_2 emitted from agriculture sector is generally considered nearly neutral, being associated with annual cycles of C fixation by photosynthesis, followed by oxidation through respiration. Therefore, only agricultural non-CO_2 sources are generally reported as anthropogenic GHG emissions, while the land-use change CO_2 emissions are generally accounted for under forest emissions to avoid double accounting. The annual total non-CO_2 GHG emissions from agriculture in 2014 are estimated to be 5.2–5.8 Pg CO_2 eq. yr^{-1} (Fig. 10.1; FAOSTAT 2016; Tubiello et al. 2013, 2015) and comprised 10 to 12% of global anthropogenic GHG emissions. Fossil fuel CO_2 emissions from agricultural use of machinery such as tractors, irrigation pumps, and other machinery are estimated to contribute an additional 0.4–0.6 Pg CO_2 eq. yr^{-1} in 2012 (FAOSTAT 2016; Ceschia et al. 2010). However, these emissions are generally accounted for in fossil fuels (Tubiello et al. 2015). Decadal average agriculture emissions grew from 4.0 ± 0.1 Pg CO_2 eq yr^{-1} in the 1980s to 5.1 ± 0.3 Pg CO_2 eq yr^{-1} in the 2000s, reaching 5.4 ± 0.3 Pg CO_2 eq yr^{-1} in 2014 (Table 10.3; Tubiello et al. 2015). Between 1990 and 2010, agricultural GHG emissions grew by 0.9% yr^{-1}, with a slight increase in growth rates after 2005 (Fig. 10.2; Tubiello et al. 2013). Overall, the growth trend of GHG emissions form agriculture for the two decades (1995–2015) were about 1% yr^{-1} (FAO 2014; Tubiello et al. 2015). Decadal average share of agricultural emissions to total anthropogenic emissions were 12.3 ± 0.6, 11.5 ± 0.3, and 11.2 ± 0.4% for 1990s, 2000s, and 2010s, respectively (Tubiello et al. 2015). The trends observed suggest that global agriculture is becoming more efficient, producing more products with fewer emissions per unit production, mainly attributed to agriculture intensification. Therefore, agriculture intensification

Table 10.3 Decadal greenhouse gas emissions from agriculture from 1970 to 2000s (Tubiello et al. 2015; FAOSTAT 2016)

Decade/years	Total GHG	CH_4	N_2O
	Pg CO_2 eq. yr^{-1}		
1970–1979	3.5 ± 0.2	2.3 ± 0.10	1.2 ± 0.10
1980–1989	4.0 ± 0.1	2.5 ± 0.04	1.5 ± 0.08
1990–1990	4.8 ± 0.3	2.6 ± 0.02	1.9 ± 0.04
2000–2009	5.1 ± 0.3	2.7 ± 0.08	2.1 ± 0.07
2010–2014	5.4 ± 0.3	2.9 ± 0.02	2.3 ± 0.04

has reduced the C footprint per agricultural product from global agriculture, and this trend is expected to continue into the future (Bennetzen et al. 2016).

Global agriculture GHG emissions increased by an average of 1.6% yr^{-1} from 1961 to 2014 reaching 5.3 Pg C eq yr^{-1} in 2014 (Fig. 10.2; Tubiello et al. 2015). In 2000–2009 and 2010–2014, the largest contributor to agricultural emissions was enteric fermentation, which was responsible for nearly 40% of total GHG emissions, followed in respective order by emissions from manure left on pasture, synthetic fertilizer use, biomass burning, rice cultivation, and manure management systems (Fig. 10.2; FAOSTAT 2016). The global disaggregated GHG emissions from agriculture covering CH_4 and N_2O emissions, and estimates for enteric fermentation, manure management, rice cultivation, crop residues and savannah burning for CH_4, and synthetic fertilizers, manure management, manure deposited on pastures during grazing, manure applied to cropland, crop residues, crop residues and savanna burning, and cultivation organic soils for N_2O (Fig. 10.3). The enteric fermentation is the dominant source of CH_4 emissions, accounting for as high as 70% of CH_4 emission (Figs. 10.1 and 10.3), and manure is dominant source of N_2O (Fig. 10.3). Global emissions of enteric fermentation grew from 1.4 to 2.1 Pg CO_2 eq. yr^{-1} between 1961 and 2014 with the average annual growth rate of 0.7% (FAOSTAT 2016). Between 2010 and 2014, about 75% of the enteric fermentation emissions were estimated to come from the developing countries, while between 2000 and 2010, Asia and America contributed most of enteric fermentation emissions, followed by Africa and Europe, and cattle contributed the largest share (FAOSTAT 2016). Emissions from manure, either applied in cropland as organic

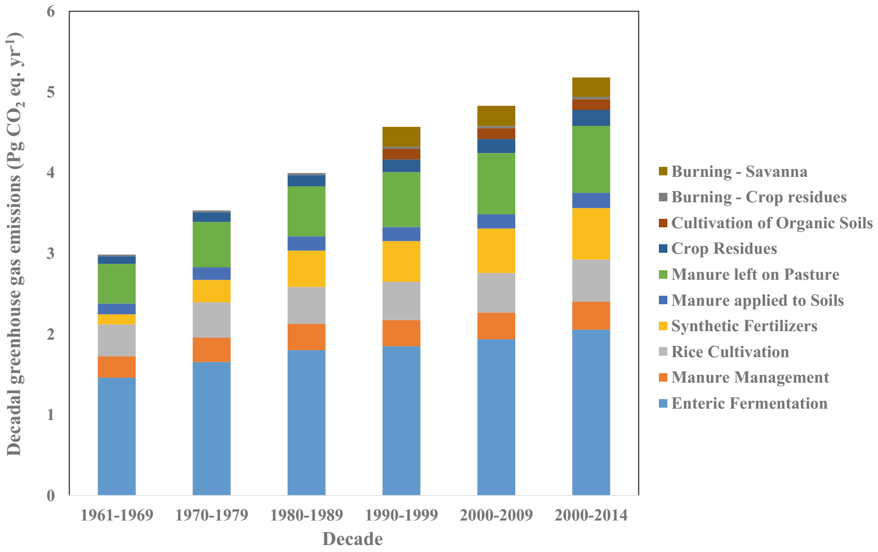

Fig. 10.2 Decadal agricultural greenhouse gases emission for the last five decades. Data from Tubiello et al. (2013), FAOSTAT (2016)

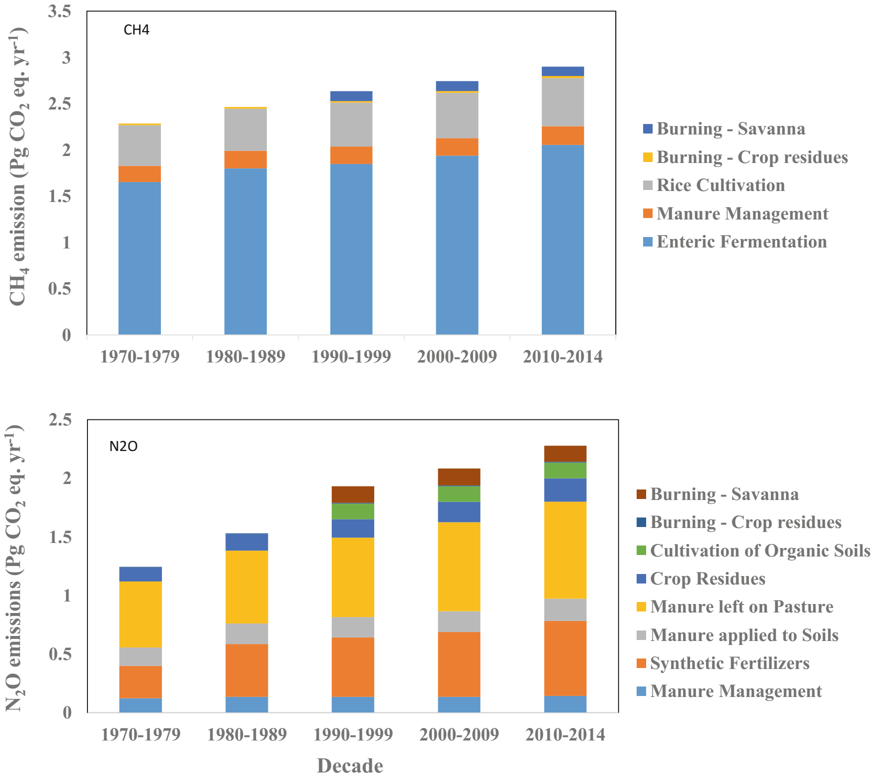

Fig. 10.3 Decadal greenhouse gas emission disaggregated by gases and sources

fertilizer or deposited on pasture grew by 1.1% yr^{-1} between 1961 and 2014, also with emissions originating from developing countries contributing the largest share (Herrero et al. 2013, 2016). Increasing emission from livestock sources is in agreement with increasing per capita consumption of livestock products, which has more than doubled in the past 40 years (FAO 2009). Increasing human population, incomes, and urbanization are projected to drive the consumption of livestock products and the agriculture GHG emissions from livestock production for the first half of the 21st century (Herrero et al. 2016). Emissions from synthetic fertilizers also grew at an average rate of 3.9% yr^{-1} from 1961 to 2010, reflecting the increase in fertilizer use in croplands which increased the crop production in the second half of the 20th century. Overall, the data shows continuous increase in agricultural GHG emission trends over the last two decades, and the share of agricultural emissions to global anthropogenic emissions in 2010 was 11%, larger than that of forest (10%) (Tubiello et al. 2015).

10.4.1 Management of Greenhouse Gases Sources and Sinks

Achieving climate stabilization will require reductions in emissions of the three main GHGs—CO_2, CH_4, and N_2O, while also enhancing CO_2 sinks to actively remove atmospheric CO_2. Agricultural land-based opportunities for mitigating GHG emissions can be broadly categorized as: reducing GHG emissions, enhancing GHG removal, and displacing or avoiding GHG emissions. The fluxes of GHGs can be reduced by managing more efficiently the flows of C and N in agricultural ecosystems. Practices that deliver added N effectively to crops often suppresses N_2O emissions GHG emissions, also managing livestock to make most efficient use of feeds often suppresses CH_4 produced (Clemens and Ahlgrimm 2001; Pacheco et al. 2014). Agricultural ecosystems hold large reserve of C, mostly in SOC, and historically, these systems have lost 60–80 Pg C due to change in natural ecosystem to managed agricultural land (Lal 2004b). Some of the lost C can be recovered through improved management, thereby withdrawing atmospheric CO_2 and sequester it as biomass and also SOC. Management practices which increase photosynthetic input of C to plant biomass or slowing decomposition of stored C are considered to sequester C.

Agroforestry systems or planting of perennials on degraded land sequesters C and offset anthropogenic emissions. Forest and woodland ecosystem contain more C than pasture or arable land ecosystems (Bolin et al. 2000), arable land soils usually contain much less C than either forest or pasture (Bolin et al. 2000). Therefore, introducing trees to cropland (i.e., agroforestry systems) or grassland (i.e., silvopastoral systems) has been proposed as a mean to extend benefits of forest to farmed land. Agroforestry and also intercropped systems increase the store of C n land managed for production (Nair et al. 2009). For example, Nair et al. (2009) reported soil C sequestration of 1 Mg ha^{-1}, while Gupta reported sequestration of 3 Mg ha^{-1} in one year and 6 Mg ha^{-1} during six year-period with little difference in loamy sand and sandy clay soils. Agroforestry and silvopastoral systems contain more C than cropland, but almost all the evidence comes from tropical and subtropical soils, little research has been conducted in temperate systems (Jose 2009; Upson and Burgess 2013). There is a need to assess the potential of agroforestry and silvopastoral systems in increasing soil C in temperate. In addition to C cycle, mixed tree and crop systems will also stimulate N cycling. Increase in N_2O emission as high as 25% has been observed (Guo et al. 2009).

Conversion of biomass derived sugars to ethanol and also plant derived oils into biodiesel is a strategy to reduce use of fossil fuels and develop sustainable energy source (Chap. 12). Crop residues from agricultural lands can be used either directly or after conversion to fuels such as ethanol or diesel and displace or avoid emissions through replacing fossil fuels with sustainably produced bioenergy. Biofuels are related C sequestration in two distinct but interrelated aspects: (a) soil C sequestration through restoration of depleted SOC pool during bioenergy crop production, especially when degraded marginal lands are converted to bioenergy plantations, and (b) use of biomass-based biofuels recycles atmospheric CO_2 though photosynthesis. Bioenergy systems can cause both positive and negative effects, and their deployment needs to balance a range of environmental, social, and economic objectives that are not fully compatible. The consequences of bioenergy implementation depends on: (i) technology used, (ii) the location, scales, and pace of implementation, (iii) the land category used (i.e., forest, grassland, marginal lands, and crop lands), (iv) the governance systems, and (v) the business models and practices adopted including how these can integrate with or displace the existing land use (Creutzig et al. 2015). With choice of appropriate species and best management practices, biofuels produced from energy plantations established by dedicated crops can sequester C in soil, offset fossil fuel emissions, and reduce the abundance of atmospheric CO_2 and other GHGs.

Emissions of CO_2 can also be avoided by agriculture practices that prevents the cultivation of new land under natural vegetation—grasslands, forests, or other non-agricultural vegetation (Foley et al. 2005; Foley et al. 2011). Because arable soils usually have much lower SOC content than the equivalent soil under forest or grass, preventing cultivation of new lands under natural vegetation and also converting arable land to grassland or forest will almost always lead to accumulation of SOC (Guo and Gifford 2002). By implication therefore, changing from annual to perennial crops should also lead to increase in SOC. In general, perennial plants store more C in soils than annual plants because the annual cycle of cultivation does little to maintain C storage. Because they live longer, many perennials invest in deep extensive root systems that are efficient in scavenging for nutrients and water as well as transferring C into deeper soil layers. Also, perennial vegetation receive fewer pass of machinery, therefore, consuming less energy because perennial systems are more diverse and receive fewer sprays that consume fossil fuels in their manufacture. However, currently there are no perennial crops that produce adequate grain yields. Carbon accumulated in soil plus vegetation after land use change from arable to forest, grassland, or perennial crops results from photosynthesis by newly established vegetation. Some of the new photosynthate is transferred to soil through roots and litter-fall. While some is rapidly decomposed and returned to the atmosphere as CO_2, but a fraction is stabilized in soil and becomes component of SOM. A part of newly formed SOM will be transformed into stable fraction with half-lives of decades to centuries in soil (Dungait et al. 2012). Table 10.4 shows approximate global area covered by different soil orders and the estimated SOC pool content of each soil order.

Croplands are often intensively managed, and therefore they offer opportunities to impose practices that reduce emission of and sequester GHGs. Some mitigation practices for croplands are presented in Table 10.5. Agronomic practices that increase crop yields and produce higher crop residues input can also lead to increased C storage in cropland soils. These include: using improved crop varieties, extending crop rotations and notably those which incorporate perennial crops and allocate more C below-ground, avoiding or minimizing bare fallow, applying appropriate amount of N fertilizer and avoid applying excess of immediate crop N requirement, adding nutrients to correct deficiencies, converting to reduced or no-tillage practice, and avoiding burning of crop residues (Smith and Gregory

Table 10.4 Soil carbon pool distribution among soil orders of the global ice-free land surface (Eswaran et al. 1993)

Soil order	Global land area		Tropical land area	
	Area cover (1000 km^2)	Soil organic pool (Pg C)	Area cover (1000 km^2)	Soil organic C pool (Pg C)
Alfisols	18,283	127	6411	30
Andisols	2552	78	1683	47
Aridisols	31,743	110	9117	29
Entisols	14,921	148	3256	19
Histosols	1745	357	286	100
Inceptisols	21,580	352	4565	60
Mollisols	5480	72	234	2
Oxisols	11,772	119	11,512	119
Spodosols	4875	71	40	2
Ultisols	11,330	105	9018	85
Vertisols	3287	19	2189	11
Other soils	7644	18	1358	2
Total	135,215	1576	49,669	506

2013). Bare soil is prone to erosion and nutrient leaching, and also contains less C than the same field under vegetation. One of the solution is to plant cover and catch crops which cover the soil in between the main crop or in fallow periods. Applying N fertilizer at the right time and placing it more precisely in soil can minimize N_2O emissions while also increasing crop productivity. However, the benefits from N fertilizers can be offset by higher N_2O emissions and CO_2 emissions from fertilizer manufacture (Henault et al. 2012). Reducing reliance on fertilizers by adopting cropping systems such as use of rotations with legume crop has high mitigation potential. Reducing tillage by adopting no-till or reduced tillage increases the C retention in soils. Overall, cropland management offers mitigation potential up to about 1.45 Pg CO_2 eq yr^{-1} (Smith and Gregory 2013).

Land management practices which enhance biomass production and SOC storage increase terrestrial C sequestration. Any land use practice that disrupts the prior long-standing balance of C or biomass inputs and decomposition will induce shift in C stocks. Land use change is the biggest disturbance—for example, converting grassland or forest land to arable cropland results in loss of SOC (Six 2013), because disturbance stimulates SOC decomposition, and C inputs to soils is reduced (Lal 2011). The overall intent of farming is to export C, therefore, stocks of C remaining in cropland soils continue to decrease with the continued C export as harvested crops, at least until new, smaller steady state equilibrium of soil C is established. Soils that have been depleted of organic matter through land use and land management practices that are inadequate to preserve SOC over the past decades to centuries—such as soil erosion, excessive tillage and overgrazing provide an opportunity to gain back significant amounts of C through application of best management practices (BMPs) including reduced tillage (especially no-till), erosion control with establishment of perennial vegetation, pasture improvement, introduction of high-yielding crop varieties, crop intensification, crop rotations, cover crops, weed control, and optimal nutrients and water management. These management practices either alter the amount of C entering the soil or protect C remaining in the cropland soils and favor C accrual through multiple mechanisms. It has been estimated that 45 Pg C could be sequestered in agricultural soils over 50–100 year span by applying improved agricultural practices (Cole et al. 1997). Terrestrial C sequestration with BMPs can be economically scaled up to achieve sequestration rates of 0.5 Pg C yr^{-1} by 2040, with one third (0.17 Pg yr^{-1}) accounted for by soil C sequestration and the remainder by reforestation (Thomson et al. 2008). Global integrated assessment estimates a conservative accumulation of terrestrial sequestration of 23–41 Pg C during the next century (Thomson et al. 2008).

The BMPs in agricultural lands provide additional opportunities for emission reductions. Agriculture releases significant amount of CH_4 and N_2O as well as CO_2, and the emissions of these gases can be reduced by managing the flows of C and N efficiently in agricultural ecosystems. The practices which reduce CH_4 and N_2O emissions brings the added value of minimum risks or reversal, since the avoided CH_4 and N_2O emissions are permanent. Activities that can contribute to significant reduction in CH_4 and N_2O include: (i) using improved regulation of flooding regimes in rice paddies with the drainage in the middle of growing season, and (ii) reducing or avoiding burning of agricultural residues, and improved timing and precision delivery of N fertilizer (Table 10.5). The technical potential for agriculture to reduce CH_4 and N_2O is high, it also contributes economically to minimize fertilizer losses while minimizing its contribution to climate change. The potential of mitigation for controlling CH_4 and N_2O emission is estimated at 8 Pg C equivalent by 2050 (Smith et al. 2014). Also, restoration of organic soils that are drained for crop production increases C sinks and has large potential, but currently remains an expensive undertaking (Smith et al. 2014). Combined mitigation potential of about 2.0 Pg CO_2 eq yr^{-1} exists through avoiding wetland drainage and carrying out erosion control measures (Smith and Gregory 2013).

Agricultural expansion has had tremendous impacts on habitats, biodiversity, C storage and soil conditions (Foley et al. 2005). A meta-analysis study across different climatic zones that compared the effects of land use changes on SOC indicated that conversion of forests to croplands resulted into SOC losses ranging from 24 to 54% of that under the forest cover. In contrast, C substitution of croplands by other land uses such as forest regrowth, tree plantation, grassland, or pasture resulted in an increase of SOC ranging from 18 to 53% (Wei et al. 2014; Barcena et al. 2014; Don et al. 2011; Poeplau et al. 2011). Avoiding emissions from land use change such as deforestation or cultivation of grasslands is one of the most immediate and large opportunities available for mitigating emissions from agriculture. For example, global forest conversion into other land uses was 13 Mha for the period between 2000 and 2010 (FAO 2015), with a gross deforestation emission flux of 2.8 ± 0.5 Pg yr^{-1}, with net land use change emissions of 1.0 Pg C yr^{-1} after accounting for forest regrowth in abandoned agricultural lands and other lands (Pan et al. 2011; Le Quéré et al. 2015, 2016). Worldwide, agriculture has cleared or

Table 10.5 Agricultural based climate mitigation activities

Component	Activities	Benefits	Risks	References
Conserve and increase biomass production	• Afforestation/reforestation • Deforestation avoidance • Reduce slash and burning agriculture • Improve forest fire management set aside land • Higher use of wood products	• Biodiversity conservation • Improved soil quality • Improved hydrological regulations • Reduced soil erosion	• Non-permanence and therefore • Risk of reversal • Saturation • Decreased water availability of other uses	Kindermann et al. (2008), Jackson et al. (2008), Lenton (2010), Galik and Jackson (2009), Aragao and Shimabukuro (2010), Smith et al. (2008)
Conservation and increasing soil C	• Reduced or no tillage • Improved water management • Restoration and rewetting drained tropical and cool peatlands • Restoration of degraded soils • Biochar application	• Increased fertility and water retention capacity • Increased biodiversity • Improved rangelands	• Reduced productivity • Increased pests • Reduced agricultural productivity (wetland restoration)	Smith et al. (2008, 2014)
Plant management	• High input carbon practices such as improved crop varieties, crop rotation, use of cover crops perennial cropping, agriculture biotechnology • Improved N use efficiency through type, timing, and precision application • Fertilizer use to increase yield and residue input	• Increased crop yield per unit area • Increased soil C storage	• Increased N_2O emissions	Burney et al. (2010), Conant et al. (2007)
Reducing CH_4 and N_2O emissions from crops, grazing lands, and livestock	• Improving paddy rice water management • Improving manure management • Precision delivery of fertilizers • Timing of fertilizer application • Improving forage quality • Managing livestock density	• Reduced water pollution • Potential for land intensification leading to land available for other uses	• Potential for reduced productivity	Schulze et al. (2009), Tian et al. (2015), Kirschke et al. (2013), Smith et al. (2008)

(continued)

Table 10.5 (continued)

Component	Activities	Benefits	Risks	References
Bioenergy production	• Use of annual and perennial crops and residues for energy • Other energy products to replace fossil fuels	• Production of domestic and industrial energy • Use of wood byproducts means no waste	• Low efficiency and limited GHG savings • Residues needed for soil fertility	Adler et al. (2007), Fargione et al. (2008), Somerville et al. (2010)
Biofuel for transportation	• Ethanol and biodiesel from food crops to replace fossil fuels • First generation biofuels—sugarcane, corn, rapeseed, palm oil • Second generation biofuels—microalgae	• Liquid fuels for transport from crops • Better GHGs benefit with energy and nutrient recycling,	• Competition for food versus energy, increased land competition • Some crops have small GHG saving • Nutrients pollution and N_2O emissions	von Blottnitz and Curran (2007), Fargione et al. (2008), Lapola et al. (2010), Lam and Lee (2012)
Waste products	• Generation of heat and electricity from industrial processes • Biogas from manure and landfills for electricity and heat	• No land competition • Reduced CH_4 emissions from landfills and livestock systems	• Potential for promoting waste production • Increased pollution to waterways	Smith et al. (2014), Chum et al. (2011)

converted 70% of grasslands, 50% of the savanna, 45% of the deciduous forest, and 27% of the tropical forest biome (Ramankutty et al. 2008). About 70% of GHG emissions from land use change comes from the tropics, illustrating the large mitigation potential in the tropics. However, it is a big challenge to reduce deforestation in tropics and achieve this potential, due to increasing human population, which is projected to occur largely in developing countries, mostly in tropical regions of the world, and also increasing demand for food and fodder. As a response to this increasing demand, United Nations Framework Convention on Climate Change (UNFCCC) has created a financial incentives for developing countries to reduce emissions from deforestation and forest degradation (REDD + initiative) so that C storage is maintained or increased in forests (Kindermann et al. 2008; Araya and Hofstad 2016).

Estimates suggest that future C sink loss resulting from deforestation could lead to additional 95 Pg C increase in atmospheric CO_2 by 2100, which is equivalent to more than 45 ppm increase in atmospheric CO_2 or >10% of the present atmospheric concentrations (Gitz and Ciais 2003). Thus, protecting forests and enhancing afforestation and forest regrowth will greatly increase the biological mitigation potential. Forest protection also has additional beneficial climate cooling effects through cycling of water. Large amounts of water returns to the atmosphere through transpiration and canopy evaporation, which support the production of convective clouds and rainfall, both of which have cooling effects on climate (Jackson et al. 2008).

Land use change emissions are often allocated to forest, even though 90% or more of emissions from land use change are driven by agricultural activities (Foley et al. 2011; Houghton 2012). Higher crop yields on land areas already cultivated are likely to induce lower CO_2 emissions than expanding the agricultural land to natural vegetation through land use change (Burney et al. 2010; Tilman et al. 2011). Afforestation is one of the viable options for C sequestration in terrestrial ecosystems (Lamb et al. 2005). Afforestation and forest regrowth on abandoned agricultural land has increased the C sinks outside the tropics such as in North America (Houghton et al. 1999), Europe (Bellassen et al. 2011), and China (Wang et al. 2007) over the past century, indicating that enabling abandoned agricultural lands to regrow forests will continue to enhance terrestrial C sinks. Some of the forest gains in developed countries have been achieved by increasing the fraction of food and wood products imported from developing countries, leading to reduced forest cover and C sinks in these regions (Karstensen et al. 2013; Dalin and Rodriguez-Iturbe 2016). In addition, the C sinks will continue to decline in the future as less fertile land is being abandoned and new forests reached maturity are harvested (Nabuurs et al. 2013; Wear and Coulston 2015). As a result, the long-term C sequestration potential of this option remains limited, particularly in areas not previously forested or if the plantations are not associated with the production of bioenergy or wood products. The estimated global cumulative avoided emission through avoiding land use change, reforestation and afforestation of abandoned agricultural land ranges from 10 to 22 Pg C by 2050 (Canadell and Schulze 2014).

Change in structure of livestock production systems that incorporates policies for reducing the demand for animal protein might also contribute to reduction of livestock GHG emissions. Other animal-based GHG mitigation practices with potential for livestock emissions include: (i) using feed additives such as dietary lipids or inclusion of concentrate feed to decrease CH_4 emissions from enteric fermentation, (ii) improving feed quality and digestibility by increasing digestible feed intake to reduce GHG emission from rumen fermentation—i.e., inclusion of energy-dense feeds such as cereal grains (Hristov et al. 2013), (iii) enhancing manure management, i.e., improving animal feces and urine chemistry through diet and also storing manure slurries appropriately to minimize volatilization or runoff, timing of manure application to match crop nutrient demand, as well as avoiding application before rain decreases N_2O emissions (Hristov et al. 2013), (iv) increasing animal productivity through improved animal husbandry practices is one of the effective strategy to reduce GHG emissions per unit of livestock product (Hristov et al. 2013), (v) increasing soil C sequestration in grasslands through grazing land management that affect species composition of forage consumption, nutrient and water inputs and fire control (Conant and Paustian 2002), and (vi) increasing pasture and crop productivity through practices that promote structure changes in livestock sector (Herrero et al. 2016). Grazing land management offers mitigation potential of up to about 1.35 Pg CO_2 eq. yr^{-1} (Smith and Gregory 2013) through techniques such as reducing grazing intensity or reducing the frequency and intensity of fires. These measures typically lead to increased tree and shrub cover resulting in CO_2 sink in both soil and biomass.

Restoration of degraded crop and pasture lands and rebuilding its SOC stocks has a large theoretical potential (Smith et al. 2007). Croplands and grasslands cover more than a third of the global ice-free land, and predominantly exist in semi-arid regions of Africa, Australia, China, and South America. Historically, croplands have lost a third to half of the SOC stocks due to tillage management and associated disturbances (Lal 2004b), and some of this SOC can be recovered through improved management thereby withdrawing atmospheric CO_2. Practices that increase the photosynthetic C input and slow the return of stored C through respiration or fire will increase stored SOC and build C sinks. However, C gains in these lands is subject to reversibility as a result of drought and fire risks. An estimated mitigation potential of 8.0 Pg C is projected by 2050 under favorable C pricing (Smith et al. 2007). Additional climate change mitigation opportunities exist from the demand side of agriculture, including changes in diets and reducing food wastes and losses in food supply chain (Smith et al. 2013, 2014).

Bioenergy production is also one of the attractive mitigation, because it can replace fossil fuel use (Chap. 12) as well as restoring degraded lands while increasing SOC stocks. The CO_2 released from the biofuels during their combustion is of recent atmospheric origin, and the net benefit of biofuels is equal to fossil derived emissions displaced minus any emissions from their production, transportation and processing. Shorter rotation cropping and harvest of residues contributes to increased bioenergy. The capacity of bioenergy crops to provide increased energy security for some countries exist, but the magnitude of the net climate benefits, the potential competition for other land uses, and long-term sustainability of large-scale biomass production need careful analysis and consideration. The current first generation biofuels produced from food crops—sugarcane, corn, sugar beet, and sweet sorghum for ethanol; rapeseed, soybean, palm oil, and Jatropha for biodiesel show ranges of GHG lifecycle analyses ranging from more than 60% for sugar cane in Brazil to less than 30% reductions for some rapeseed-biodiesel systems in Europe and corn ethanol in USA (Adler et al. 2007; von Blottnitz and Curran 2007; Lisboa et al. 2011). In some cases, N_2O emissions resulting from fertilizer use and emissions resulting from clearing of natural ecosystems results in highly reduced or no climate change mitigation benefits. Many of the current first generation biofuels which their production involves transformation of native ecosystems do not yield net GHG emission savings when land use change emissions are included in lifecycle analysis (Lapola et al. 2010; Fargione et al. 2008; Searchinger et al. 2008). Second generation biofuels have more favorable GHG savings potential than many food-based crops, especially if produced from marginal lands or with low inputs (Somerville et al. 2010; Davis et al. 2012).

10.4.2 Technologies for Carbon Sequestration Enhancement

Terrestrial C sequestration is often seen as win-win opportunity (Lal 2004c; Srivastava et al. 2012) due to removal of atmospheric CO_2 while simultaneously improving soil productivity in croplands. However, C gain is finite, and can continue only for few decades, as C build up in soils is slowed and decomposition rate is increased, and eventually converging upon C inputs and halting further gains (van Groenigen et al. 2014). It is estimated that the contribution of current methods for C sequestration tapers off toward the end of the century (Thomson et al. 2008), primarily if sequestration methods are adopted on all available land. The only way to boost the terrestrial contribution in later periods would be through development and deployment of advanced technologies. C inputs in arable agricultural lands are often less than those in the corresponding natural ecosystems, both due to smaller NPP and also the export of photosynthesized C with crop harvest (Krausmann et al. 2013). Consequently, without drastic yield enhancement or cessation of harvest as in ‘set-aside’ lands, restoring C to levels approaching pre-agricultural soils may have numerous co-benefits but cannot by itself mitigate climate change. Therefore, C sequestration in soils and biomass is generally seen as ‘buying time’ for other mitigation strategies to emerge and take effect (Post et al. 2012). In addition, practices that promote SOC storage in soils may also stimulate N_2O emissions, partially offsetting the CO_2 removal from the atmosphere (Conant et al. 2005). Similarly, planting grasses that can sequester C may favor grazing, which results into increase in CH_4 emitted by ruminants or N_2O from animal manure and offset some of soil C accrual (Bellarby et al. 2013). Soil C accrual may cease, but elevated N_2O and CH_4 emissions can sometimes persist for long time, and early benefits of SOC sequestration could increasingly be offset by other emissions. Furthermore, C replenished is also susceptible to future loss from regressive practices or evolving conditions such as future warming, although the response is complex and difficult to predict (Schmidt et al. 2011). Furthermore, stimulated plant growth and C input from CO_2 fertilization may limit C gains by promoting decomposition (van Groenigen et al. 2014). Therefore, storing more C in soils remains a worthy, laudable endeavor, but only as one of many concurrent interwoven services granted by land (Janzen 2015).

Technical developments can be used to enhance terrestrial C sequestration. Some of technologies with the potential to impact terrestrial C sequestration include: (i) biotechnology, (ii) biochar creation and application to soils, and (iii) deep-soil sequestration. The genomics and biotechnology provides an opportunity to identify genes, enzymes, biochemical pathways, and regulatory processes that underlie rate-limiting steps in C acquisition, transport, and its fate in plants, thereby yield new approaches to enhance NPP and terrestrial C sequestration. Therefore, an investment in plant and biotechnology could harness new approaches to increase biomass production in agricultural crops, also produce fast-growing trees in managed plantations. Research focusing on targeted improvements in light-use efficiency and photosynthesis (Ort et al. 2015), root growth and acquisition of nutrients and water (Hirel et al. 2007), and by overcoming constraints imposed on plant productivity by temperature and drought (Tuberosa and Salvi 2006; Sadras and Richards 2014) could increase crop productivity as well as NPP. For most terrestrial plants, availability of water usually is the main productivity limitation (Lobell et al. 2014), and the inability of photosynthesis to efficiently use high midday light intensities strongly limits productivity (Murchie and Niyogi 2011). Light is essential for photosynthesis and supports most life on Earth. However, light intensity and spectral quality are highly variable in space and time of the day, season, geographical location, climate and the position of leaf within canopy and cells within leaf (Murchie and Niyogi 2011). There regulatory mechanisms are highly integrated with photosynthesis itself, and emerging evidence indicate that when these processes are altered, the ability of plants to assimilate C over long time periods and produce biomass are affected. There are only few options for dramatically reducing the amount of water required by crops to grow however. Root architecture the spatial arrangement of root system are important in agricultural and natural systems (Hirel et al. 2007; York et al. 2013). Genome-enabled increases in the production of plant biomass would, all else being equal, translate to enhanced input of C to soils via shoot and root litter, increasing the storage of C in terrestrial ecosystems. Gains in C sequestration are also likely to be realized by understanding how genes and proteins that control the chemical composition of litter could impact the rates and magnitudes of C sequestration.

Improved solar energy conversion (photosynthetic efficiency) has played little role in improving productivity. For example, the progenitors of modern crop plants evolved from and are adapted to atmospheric CO_2 concentration of $\sim$240 ppm, and therefore, accelerated rate of ribose 1,5 bisphosphate carboxylase-oxygenase (Rubisco)-catalyzed carboxylation at current CO_2 concentration of >400 ppm has led to kinetic limitation in the generation of CO_2 acceptor molecule—ribulose 1,5 bisphosphate (RubBP), which will become increasingly limiting as CO_2 concentration increases further (Zhu et al. 2004). Attempts to increase rates of photosynthesis through genetic engineering have focused on accomplishing this goal by reengineering or increasing the total amount of Rubisco in leaves (Suzuki et al. 2007; Parry et al. 2007) and also by actively concentrating CO_2 at the site of Rubisco (Price et al. 2013). Rubisco catalyzes the photosynthetic assimilation of CO_2 into organic compounds, and is often a rate limiting step in photosynthesis at the top of canopy in field grown crops (Carmo-Silva et al. 2015), optimizing its functionality has large implications regarding the improvement of plant productivity and resource use efficiency (Whitney et al. 2011). Rubisco is central to plant productivity and much research has been directed towards improving its properties. Contrary to original expectations however, research has been met with mixed success. The lack of viable chloroplasts transformation protocols for many crop plants has hindered direct manipulation of the chloroplast-encoded large sub-unit of Rubisco (Carmo-Silva et al. 2015). Although the advanced technologies now available and the comprehensive knowledge on Rubisco properties, function, regulation and interaction exist, the goal of improving Rubisco, and therefore, photosynthesis has not been attained. Additional research seeking to increase photosynthesis and plant productivity not by modifying the amount but by optimizing the distribution of resources between enzymes of C metabolism and/or by altering the kinetic properties of the Rubisco enzyme itself is needed. Theoretical analyses suggest that expressing Rubisco as having either a higher specificity for CO_2 relative to O_2 or a higher maximum catalytic rate of carboxylation per active site could increase photosynthetic C gain by 25% or more in C_3 plants (Zhu et al. 2004).

Studies of decomposition of OM in peatlands have shown inhibition of the enzymes responsible for decomposition by phenolic compounds (Zibilske and Bradford 2007; Toberman et al. 2008; Sinsabaugh 2010). These studies suggest an important role of phenolic compounds in C cycle: (i) few enzymes degrade these abundant materials, and those enzymes that do are inhibited almost completely under certain conditions or combinations of conditions found in peat, (ii) phenolic compounds inhibit other enzymes that decompose OM in soils, (iii) many phenolic compounds bind other OM especially proteins and enzymes and reduce the availability of OM for decomposition, and also removes other enzymes such as hydrolases that contribute to the decomposition. The studies of peat therefore, suggest that in addition to lack of oxygen, C accumulation in peat soils may be the result of restricted activity of oxidases and peroxidases that remove phenols (Whitmore et al. 2015), suggesting that OM decomposition in soil might be reduced by application of inhibitors or antioxidants. It has been proposed that the decomposition of organic residues in soil is performed by free radicals, and the antioxidants such as quinines, commonly found in soil moderate the activity by quenching free radicals (Rimmer 2006). Similarly, it has been observed that total soil C content was related to the antioxidant capacity of soils, and antioxidant capacity decreased with soil depth (Rimmer and Smith 2009). Further, organic amendments naturally containing large amounts of antioxidants decompose slowly in soils during an initial 7-day period (Rimmer et al. 2013). Therefore, there is a possibility of altering the rate of OM decomposition and increase SOC storage through manipulation of the antioxidant and other navel techniques.

10.4.2.1 Biochar (Biomass C Stabilization)

Harvestable biomass can be converted to biofuels and bio-products by thermochemical processes such as pyrolysis. Biomass C is stabilized through low-temperature pyrolysis, by heating under low-oxygen conditions while also producing liquid and gaseous biofuels (Lehmann 2007). Heating biomass with air excluded, hydrogen and oxygen are preferentially eliminated creating biologically recalcitrant C-rich char-like substances. The major products from biomass thermochemical processes are syngas, bio-oil, biochar, and tar, and yields depend on the process conditions. Syngas and bio-oil are considered as major intermediate products that can be used to create fuels alternative to conventional fossil fuels, and it can be used for various applications (Mortensen et al. 2011; Swain et al. 2011). Biochar (charred OM) can be used as soil amendment to mitigate the GHG emission and improve soil health. It is a solid material obtained from thermochemical conversion of biomass in an O_2-limited environment (IBI 2012). In addition to bioenergy production, biochar consists of stable C which is more recalcitrant and can be sequestered in soils for hundreds or even thousands of years, which allows biochar to act as C sink (Sohi et al. 2009) due to its chemical inertness and highly resistant towards degradation (Schmidt and Noack 2000). Biochar is a mixture of heterogeneous substances including labile and recalcitrant aromatic compounds, and therefore, its half-life depends on the percentage of both components. Increasing the amount of recalcitrant leads to increase in the half-life of biochar. The nature and yield of the solid product obtained depends on the feedstock and temperatures and pressures employed (Qian et al. 2015) and its porosity increases with temperature from 250 to 800 °C. Incorporating biochar into the agricultural soils could protect it from further oxidation, where, depending on the nature of the product, it may also improve nutrient- and moisture-holding properties while decomposing at a much slower rate than unconverted biomass (Gray et al. 2014). Additional benefits of biochar application includes reduction of N_2O and CH_4 emissions. The contribution of biomass carbonization to C sequestration is potentially large. However, for deployment of biochar mitigation, four variables need to be considered: (i) sustainable biomass production level, (ii) carbonization efficiency, (iii) land storage capacity, and (iv) characteristic storage time (i.e., the oxidation rate of stabilized C placed in soil). Overall, realizing the mitigation potential for biochar will be constrained by the need for sustainable feedstock acquisition. Competing biomass use options will be important influence of the production process on biochar properties. Deployment of biochar on less fertile land has the global potential abatement of 6.6 Pg CO_2 eq yr^{-1} from 2.27 Pg of sustainable biomass (Woolf et al. 2010). In near-term, meta-analysis indicates that under the experimental situations on average, biochar application enhances crop productivity by 15% but with wide range of effects (Jeffery et al. 2011; Biederman and Harpole 2013; Mukerjee and Lal 2014), probably explained by the nature and extent of pre-existing soil conditions. Biochar also has a beneficial interaction with soil N cycle, with effects on mineralization, nitrification, denitrification, immobilization and adsorption persisting at least for days to months after biochar addition to soils (Nelissen et al. 2012; Clough et al. 2013). Biochar may also suppress soil N_2O emissions in the laboratory conditions (Cayuela et al. 2013), but only limited validation of N_2O suppression has been achieved by biochar in the field over longer timeframes (Spokas 2013; Van Zwieten et al. 2013). The characteristic storage time (i.e., half-life) of biochar C in soil depends greatly on the pyrolysis process used as well as soil properties, such as temperature and pH, and likely varies for the different forms of C present in the stabilized solid. For biochar incorporated into soil, longevity may increase because of lower O_2 levels. The estimated half-life of biochar in soils has been inferred from wildfire charcoal (Lehmann 2007) or extrapolated from direct short-term observation, and values ranging from <50 to >10,000 years have been reported, but the commonly accepted range is predominantly 100–1000 years (Singh et al. 2012; Spokas 2013). Adoption of biochar as climate change mitigation remains limited, and its future use will mostly depend on predictable positive effects on crop production. Other factors limiting the adoption include lack of product standards, production costs, lack of economic incentives, production costs, and large quantities required to produce expected agronomic benefits. More research on the benefits of using repeated low dose soil inputs rather than single application at rates >10 Mg ha^{-1} which have so far been the norm are needed.

10.4.2.2 Sub-soil Carbon Sequestration

It is now believed that there is a lot more deep soil C than initially once thought, and the underlying processes inhibiting its turnover are still largely unknown (Schmidt et al. 2011; Lorenz and Lal 2005). For example, about one third (840 Pg C) of the 2344 Gt C stored in top 3 m depth of soils is located at depths greater than 1 m (Batjes 1996; Jobbagy and Jackson 2000), where O_2 concentration is low, and it is strongly stabilized by adsorption to mineral surfaces, with half-life of millennia (Trumbore 1997). Despite their low C concentrations, sub-soil horizons contribute to more than half of the global soil C stocks (Jobbagy and Jackson 2000). The OM input into sub-soil horizons occurs naturally as root litter and root exudates, dissolved OM and/or bioturbation (Rumpel and Kogel-Knabner 2011). In addition, translocation of particulate matter and transport of clay-bound OM can occur in some soil types. However, the relative importance of different sources is not known (Rumpel and Kogel-Knabner 2011). The relative importance of these sources depends on climatic parameters, soil inherent processes, and land use. For example, in humid climate conditions, higher input of dissolved OM into subsoil is expected when the podzolisation is the main soil forming process (Kaiser and Guggenberger 2000). The lower horizons of widespread, mature soils, such as Alfisols, Ultisols, and Oxisols, have a tremendous capacity to adsorb organic C because of their vertical extent, acidic pH, and abundant clay and iron oxide contents (Benke et al. 1999; Kong et al. 2005). In addition, hydrophobic OM has higher affinity to mineral sub-soils of Bs and C horizons of cool humid climate soil (Ussiri and Johnson 2004), suggesting that deep horizon soils have high sorption capacity of OC. Based on depth trends of elemental composition (i.e., decreasing C:N ratio), isotopic composition (increasing $\delta^{13}C$ values), and individual organic compounds, microbial products make up more OC in subsoil horizon than the plant compounds (Torn et al. 2002). The OM in subsoil is generally characterized by long turnover times that increases with depth (i.e., radiocarbon ages of 1000 to >10,000 years), but the reason for this remains unclear. Microbial activity may be reduced by suboptimal conditions, nutrients limitation, energy scarcity, or combination of these, making OM less accessible due to its sparse density or association with reactive mineral surfaces. Energy limitation or priming by roots exudates or dissolved OC may also play significant role (Kuzyakov 2010; Fontaine et al. 2007). Microbial biomass decreases with depth (Fierer et al. 2003; Liu et al. 2016), and microbial community composition changes to reflect an increase in substrate specialization (Kramer and Gleixner 2008). Due to lack of understanding of the mechanisms of stabilization, prediction of vulnerability of deep SOM to change is not possible with the present knowledge.

Common fertilization methods in agriculture and silviculture may, in fact, already be enhancing the downward vertical spread of OC through the soil profile with the benefit of long-term C protection. Results from sorption experiments (Jardine et al. 2006) suggest that the maximum for increasing this sequestration reservoir is 165 Pg C for each meter of soil depth. Certain N sources, particularly urea, not only enhance plant vigor but also interact strongly with soil organic materials (Sen and Chalk 1994; Ouyang et al. 1999). Mineralization and dissolution of soil organic matter is stimulated by N fertilizers, which hydrolyze to form alkaline solutions. For example, an extremely high pH (pH 9) sometimes develops in the immediate vicinity of hydrolyzing urea granules, which renders otherwise resistant humus complexes soluble and available for transport through soil horizons. Research and demonstration projects are needed to evaluate, reconcile, and optimize the tradeoffs between: (a) efforts to stabilize SOM at the surface in order to maintain a sustainable nutrient reserve, soil tilth, and optimum soil structure to support healthy plant growth such as implementation of no-till and afforestation, and (b) practices to actively disaggregate and move humus from the surface for the purpose of sending DOC deeper in the profile. To efficiently use this reservoir, however, ways of moving C from the upper horizons to greater depths are needed. Amendments with lime, urea, and phosphate fertilizers offer a possible approach, although experimental research is needed to prove its ultimate utility. In addition, the energy required to produce the amendments required needs quantification with respect to the amount of C sequestration attained. Finally, the amount of GHGs released under various environmental conditions for each amendment needs determination.

In grasslands and livestock production, improving forage quality and overall efficiency of dietary nutrient use is an effective way of decreasing GHG emissions per unit of animal product. Feed supplements with the potential to reduce enteric CH_4 emissions from ruminants include electron receptors such as nitrates, furmate, sulfates, and nitroethanes (Gutierrez-Banuelos et al. 2007; Brown et al. 2011), dietary lipids, exogenous enzymes and directly fed microbial organisms (Hristov et al. 2013). However, their long-term effects is not well-established, and some may have toxic or may not be economically viable in many developing countries. Manure management practices also have a significant potential in decreasing CH_4 and N_2O emissions. Some practices are applicable for storage—including separation of solids and liquid manures, animal dietary management, and timing of field application (Hristov et al. 2013). Overall, optimizing animal productivity remains one of the most successful strategy for mitigation GHG emissions from livestock sector in both developed and developing countries.

10.4.3 Saturation and Permanence

Sequestration in soils and vegetation and retention of existing C stocks forms a significant component of mitigation in agriculture. However, C accumulation in the biosphere cannot continue indefinitely (Gulde et al. 2008; White et al. 2009), and a new steady-state C content will follow a change in environmental conditions or management. For example, C stored in soil and tree biomass reaches new equilibrium as the tree matures or as the stocks of C saturates. As soil and vegetation approach the new equilibrium, the annual removal (i.e., sink strength) decreases until it becomes zero at equilibrium. Therefore, the amount of C that can be stored in biomass and in soil is finite, and ceases as new equilibrium is approached. This principle is clear from long-term studies which have shown that SOC does not accumulate in soil indefinitely (Johnston et al. 2009). Generally, annual rate of increase tend to be greatest in early years and very slow near the end as the soil approaches a new equilibrium. In addition, various types of C sinks have an inherent risk of reversal. Reversal can be caused by natural events that affect yield or growth, frost damage, pest infestation, or fire (Xiao et al. 2016), these effects may be short-term. However, they will affect annual incremental of C sequestration, and some may not result in permanent decline in C stocks. The change in land management leading to increased C in soil or vegetation must therefore, be continued indefinitely to maintain the increased stock of SOC (Freibauer et al. 2004). If forest is established, the C accumulated in trees will be lost if the trees are cleared (Saarsalmi et al. 2010). Similarly, if grass or legume is included in ley cropping system, at least part of the SOC is lost after plowing for the next arable phase, even though there will often be some overall increase in SOC in the long-term compared to continuous arable cropping if the ley-arable rotation is continued (Johnston et al. 2009).

Land management changes leading to increased C may either increase or decrease fluxes of other GHGs such as N_2O or CH_4. In many situations these changes may be far more significant than changes in SOC stock because of the large global warming potential (GWP) of these gases (Myhre et al. 2013). Therefore small changes in fluxes of these gases can have large impact on the overall effect on climate change of a given land management. In contrast, certain types of mitigation such as avoided N_2O from fertilizer use and manure management, avoided CH_4 emission from livestock through diet change or displacement of fossil fuels by bioenergy are permanent, since once the emission is avoided it cannot be re-emitted. The C content of a soil is volatile and is difficult to monitor and measure accurately. It is also heterogeneous and varies over time, even in the absence of changes in land management. Protecting carbon that is already in the biosphere provides one of the most important opportunities (Sathaye et al. 2006). Leakage is likely to be less for changes in agricultural methods, although an increase in agricultural productivity could be reflected in a reduction in the total amount of land being tilled.

10.5 Conclusions

Soils are subject to varying degree of direct and indirect anthropogenic disturbance, and constitute a major global change driver. However, distinguishing natural terrestrial GHG emissions from direct and indirect human induced GHG emissions is not a straight forward, but some human activities that have clear impacts include land use change, land management, and land degradation. As a result of global land and soil disturbances and other anthropogenic activities, the atmospheric GHG concentrations have increased significantly since industrial revolution. Agriculture is the sector of the economy that is most vulnerable to the effects of global warming, such as more variable rainfall and more extreme weather-generated events. Similarly, agriculture and the associated land use change are among the principal contributors to climate change, accounting for about a quarter of the global GHG emissions. The projected increase in demand for food and bioenergy by 2050 have a profound implications for the pressure that agriculture presents on forests and other natural ecosystems, especially in the tropics. Land-based biological C mitigation strategies are considered an important and viable pathway towards climate stabilization. Increasing agricultural productivity, enhancing its resilience to climate change, reducing the GHG emissions that comes from the agriculture sector, and also sequestering SOC in agriculture soil is of vital importance, and it requires alternative sets of agriculture practices. This requires sustainable land management involving the implementation of best management practices that enable humans to maximize the economic benefits from the land while also maintaining and/or enhancing the ecosystem services that land resources provide. Terrestrial C sequestration could be an important and immediate option for creditable GHG mitigation while the long-term options of no-C or low-C fuel sources take effect. The cost of attaining atmospheric CO_2 stabilization will be significantly reduced even if the existing techniques of terrestrial C sequestration are more aggressively utilized. Soil C has direct correlation with soil quality and soil health. The GHG emissions from land use change can be reduced by sustainable intensification of agriculture and livestock production, improving livestock management, and also increasing SOC sequestration in soils and biomass. In addition, emissions from energy can be reduced by substituting fossil fuels by bioenergy. Other agriculture mitigation options includes reducing losses and waste of food, changes in diet to lower C footprint diets. Currently available land-based biological mitigation have, and will have important role in achieving climate stabilization, largely from reduced emissions from land use and land use change and from substitution of fossil fuels with sustainably produced bioenergy. With current technologies, the potential for land mitigation is significant, but relatively small compared with overall mitigation requirements for climate stabilization. Future growth in bio-based mitigation will depend on the success of developing systems that minimize the requirement for additional land and nutrients, while contributing to sustainable intensification of land. Advancements are required in both technological innovations that can lead to increasing photosynthetic potentials to increase NPP.

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Chapter 11
Global Forests Management for Climate Change Mitigation

Abstract Forests are the dominant terrestrial ecosystem occupying approximately 30% of the Earth total land area. They play an important role in the global carbon (C) cycle, and the mitigation of CO_2 emission due to its large storage of soil organic C (SOC), a large part of which is stored in soils. Due to their dominance, forests management has gained much interest in science and policy discussions as one of the important options to mitigate climate change. Global forests are increasingly affected by land use change, fragmentation, changing management objectives and degradation. The area under global forests has declined by 3% from 1990 to 2015, but the area of planted forest has increased in all regions of the world and now accounts for nearly 7% of global forest land estimated at 3999 million hectares (Mha). The area of primary forests which is typically defined as lacking direct human influence, is about 34% of the total forest land, based on country reports, but this area is declining, especially in South America and Africa because of human-caused fragmentation and degradation. About 5% of global forests are plantations generally used for commercial purposes. Globally, timber production has remained stable since 1990, but forest used for non-wood forest products indicates that harvesting is taking place on a smaller proportion of total forest area. Based on trends in the area of managed forest and regional studies, historical and current forest management has been a significant determinant of current carbon stocks in forest. The established forest currently offset 30% of global emissions of CO_2 from fossil fuel combustion, and there are mitigation opportunities involving forests that could increase the gross terrestrial C uptake from about 4.0 to 6.2 Pg C annually. Diversifying use of forest land may have significant consequences for maintaining or increasing the current rate of terrestrial C sequestration. Indirect human influences such as increasing atmospheric CO_2 and climate change, along with the direct effects of land management and projected increasing demand for wood biofuel, are likely to become increasingly important elements that influence land management strategies and the role of forests in the global C cycle and future climate mitigation.

Keywords Forest resources · Deforestation · Afforestation · Land use change · Sustainable forest management · Primary forest · Gross primary productivity · Net primary productivity

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Contents

11.1 Introduction

Forests, the dominant terrestrial ecosystem on Earth, are distributed across boreal, temperate, and tropical zones and account for 80% of Earth total biomass (Kindermann et al. 2008). They also account for 75% of the terrestrial gross primary production (GPP) (Beer et al. 2010). They are locally and globally important ecosystems that provide habitat, timber resources, carbon (C) storage, recreational opportunities, as well as multiple ecosystem services and cultural and spiritual values (Hicke et al. 2007; McKinley et al. 2011; Miura et al. 2015). Forests harbor the majority of species on Earth (Jackson et al. 2005) and contain more C in the biomass and soils than that resides in the atmosphere (Pan et al. 2011; Bellassen and Luyssaert 2014). In addition to providing valuable services to society, forests also play an important role in the global C cycle. Compared to other terrestrial ecosystems, forests store the largest quantities of C per unit land area (Poeplau et al. 2011). As a result, forests represent one of the largest, most cost-effective mitigation for climate change solutions available currently. The C storage capacity in forests could be improved through afforestation or decreased by deforestation (Wei et al. 2014). For example, afforestation of croplands results in soil C accumulation at a rate of 0.38 ± 0.04 Mg ha^{-1} yr^{-1}, lasting for more than 100 years (Poeplau et al. 2011). Global forests are also increasingly affected by deforestation and land use change, fragmentation, changing management objectives, degradation, as well as responding to changes in atmospheric composition especially increasing CO_2 concentration, N deposition tropospheric O_3, and climate change. The response to these concurrent factors will determine the sustainability of many traditional services provided by forests such as timber production, watershed protection, as well as future C sequestration.

Forests contribute to soil formation and water regulation, and are estimated to provide direct employment to as many as 10 million people and source of livelihood to millions more (FAO 2010). It is estimated that more that 200 million people from the world's poor communities rely directly on forests for energy, shelter, and their livelihood (Hirsch 2010). Clean water is becoming more recognized as one of the most important environmental services provided by forests. At least one third of the world's largest cities draw a significant proportion of their drinking water from forested areas (FAO 2013). In 2015, 1002 million hectare (Mha) or 25.1% of world's forests were primarily designated for protection of soil and water, also an additional 25.4% is managed for ecosystem services (Miura et al. 2015; FAO 2015). In the context of resilience to climate change, forests are also recognized to play an important role in minimizing the risks of natural hazards such as landslides and local floods, creating resilience as well as adaptation to climate change.

Net primary productivity (NPP), defined as the difference between accumulative photosynthesis and accumulative autotrophic respiration by green plants per unit of time and space, is the important parameter for quantifying the exchanges of energy and mass by vegetation (Running and Coughlan 1988). In general, forest ecosystem NPP accounts for 35% of global and 65% of terrestrial ecosystem NPP, respectively (Waring and Schlesinger 1985; Gower et al. 1996). Forest ecosystems contains up to 80% of all aboveground terrestrial biomass C and approximately 40% of all belowground terrestrial C (Dixon et al. 1994). Compared to other terrestrial ecosystems, forests store the largest quantities of C per unit surface area of land (Poeplau et al. 2011), and therefore, they are the major component of Earth C cycling. Thus, afforestation increases C storage capacity, while deforestation decreases terrestrial C storage capacity (Poeplau et al. 2011; Wei et al. 2014). A slight change in NPP of forests will significantly influence atmospheric CO_2 concentration and, consequently, climate change. The annual CO_2 exchange between forests and atmosphere through photosynthesis and respiration is estimated to be ≈ 50 Pg C yr^{-1} (Beer et al. 2010), and an increase in soil respiration would increase the CO_2 emission from forest ecosystems.

The net C accumulation in forest ecosystem over decadal time frame is more influenced by disturbances than climate and atmospheric CO_2 concentration (Pregitzer and Euskirchen 2004). Therefore, understanding how disturbances and stand age interact could provide fundamental knowledge of the terrestrial C cycle. The C stored in forest ecosystems over the long term will be released rapidly and in considerable amounts into the atmosphere following disturbances (Page et al. 2002). In forests, time since disturbances (i.e., forest age) and forest structure are critical factors determining forest ecosystem C storage and fluxes (Song and Woodcock 2003; Litvak et al. 2003; Kashian et al. 2006; Goulden et al. 2011). Generally, forest C cycling is influenced by forest age—including biomass of coarse woody debris (Bond-Lamberty et al. 2002; Li et al. 2012), forest stand water use (Delzon and Loustau 2005), SOC (Peltoniemi et al. 2004), live biomass increment and litter decomposition (Bradford et al. 2008), size structure, NPP, and net ecosystem productivity (NEP)/net biome productivity (Hoshino et al. 2001; Litvak et al. 2003; Song and Woodcock 2003), and other biophysical properties (McMillan and Goulden 2008). Younger forests are inherently more productive than older forests (Ryan et al. 1997) and model predictions also show that successional changes influence rates of NEP through time (Thornton et al. 2002). As a result of the high variation in stand age in large forest areas, efforts to estimate ecosystem C fluxes must take into account forest age structure (Song and Woodcock 2003), especially the quantitative analysis of forest NPP changes with stand age among forest types (Chen et al. 2003) to improve the reliability. In general, quantitative research on the temporal trends of C balance related to stand age at regional and/or global scales is rare due to lack of long-term records of disturbances, and most process-based models ignore the effects of disturbances on NPP and terrestrial C sequestration (e.g., Dean et al. 2004; Thornley and Cannell 2004), mainly because of the lack of spatial data on NPP and age distributions. The C cycling and stand age relationships developed on single species have indicated that biomass accumulation peaked within 40–60 years, while a meta-analysis of published chronosequence data to explore the dependence of forest NPP on age by age classes for tropical, temperate, and boreal forest biomes suggested that peak NPP in boreal forest occurred in the 71–120 year age class while older forests >120 years were generally less productive (Pregitzer and Euskirchen 2004).

Over the past 25 years, an average of 4.6 Mha yr^{-1} of forests are cleared and converted for production of commodities including soy, palm oil, beef, and paper, falling from 7.3 Mha yr^{-1} in the 1990s (Keenan et al. 2015). In addition, infrastructure, urban expansion, mining, and fuel wood also contribute to annual forest loss. Globally, 129 Mha of natural and planted forest were deforested between 1990 and 2015, representing an annual rate of forest loss of 0.13% (FAO 2015). The net annual rate of forest loss has slowed from 0.18% in 1990s to a net annual loss of 0.08% over the last 5 years (FAO 2015). Between 2010 and 2015, there was an annual loss of 7.6 Mha and net gain of 4.3 Mha, resulting in net annual decrease of 3.3 Mha yr^{-1} occurring in every climatic domain (FAO 2015). However, the largest area of forest converted to other land uses between 1990 and 2015 was the tropical forests, and the continents with the greatest forest area loss are Africa and South America, where forest land is converted to agriculture and other land uses in response to population increase (FAO 2015).

Forestry plays central role in sustainable development, global climate change, and mitigation. Decadal land use change emission of CO_2, mainly from deforestation and forest degradation in tropical regions from 1990 to 2014 are estimated at 1.2 ± 0.5 Pg C yr^{-1}, equivalent to 16% of C emissions from fossil fuels from 1990 to 2015 (Pan et al. 2011; Le Quéré et al. 2015, 2016), which is offset by tropical regrowth, boreal, temperate, and intact tropical forests C sink. Decadal residual terrestrial C sink estimated as anthropogenic emissions from fossil fuel and land use change minus ocean uptake and atmospheric growth rate for 1990–2015 is estimated at 2.8 Pg C yr^{-1} (Pan et al. 2011; Le Quéré et al. 2015, 2016). Decadal land use change emissions declined from 1.6 ± 0.5 Pg C yr^{-1} in 1990s to 1.0 ± 0.5 Pg C yr^{-1} in 2000s, while residual terrestrial C sinks increased from 2.6 ± 0.8 Pg C yr^{-1} in 1990s to 3.1 ± 0.8 Pg C yr^{-1} in 2000s (Le Quéré et al. 2015, 2016). Concerns about the role of tropical forests in global climate change have led to the United Nations (UN) to propose a mechanism to facilitate tropical countries participation in climate change mitigation through reducing emission from deforestation and degradation and the role of conservation (REDD+), sustainable management of forests and enhancement of forest C stocks (UNFCCC 2007). Tropical forest growth amounts for a sink of 1.6 ± 0.8 Pg C yr^{-1}, which offsets significant portion of emissions (Nabuurs et al. 2007; Pan et al. 2011). Therefore, by participation in REDD+, tropical countries could turn tropical forests to a net C sink instead of source. Forests are also affected by climate change, and their contribution to mitigation strategies may be influenced by stresses resulting from climate change. Global forests also play significant roles socioeconomically by providing important goods, services, and financial values to the societies. Other co-benefits of forests include biodiversity and watershed conservation, provision of timber and fiber, as well as recreational services. Forest mitigation options include reducing emissions from deforestation and forest land degradation, enhancing sequestration rates in existing forests, providing fuel substitute for fossil fuels, and also providing wood products for more energy-intensive materials.

Plants take up CO_2 from the atmosphere and N from soil. When they grow and redistribute it among different pools including above and below ground biomass, dead tissues, and soil organic matter (SOM). CO_2, CH_4 and N_2O are in turn released to the atmosphere through respiration and decomposition of dead plant biomass and SOM or through combustion. Anthropogenic land use activities such as forest logging, conversion of forest lands and deforestation and afforestation cause changes superimposed on natural gaseous exchange fluxes. These activities can both lead to source and sinks of CO_2 in forest. Forest management activities play key role through mitigation of climate change. However, forests are also affected by climate change, and their contribution to mitigation strategies may be influenced by stresses resulting from climate change. Forest mitigation options include (i) reducing emissions from deforestation and forest degradation, enhancing sequestration rate in existing and new forests, provisioning of wood fuel as a substitute for fossil fuel, and providing wood products for more energy intensive materials. There is an increased attention to reducing emissions from deforestation as low cost mitigation option and with significant positive side effects.

Several analyses has estimated the terrestrial C sink in the range of 1.1–3.6 Pg C yr^{-1} for the 1990s and 2000s on the basis of atmospheric CO_2 observations and inverse modeling as well as land observation (Canadell et al. 2007b; Khatiwala et al. 2009; Le Quéré et al. 2009, 2015), while the budget residual, after accounting for atmospheric growth and ocean uptake suggest the land sink ranging from 2.6 to 4.1 (Le Quéré et al. 2015). Most forests of the world are recovering from a past disturbance, and there is a considerable uncertainty in the future trajectory and magnitude of terrestrial C sink, as many aggrading forests approach maturity following clear-cut harvesting a century or more ago (Birdsey et al. 2006). With these re-growing forests advancing beyond early aggrading phase of succession, an ecologically important transition will occur in which structurally and biologically simple forests dominated by short-lived early successional trees senesce and allow more complex stands comprising of longer lived, later successional species (Birdsey et al. 2006). Naturally regenerated mixed-deciduous forests in many regions especially in North America and Eurasia are leading to reemergence of later successional forests (Luyssaert et al. 2010; Wang et al. 2011). The objectives of this chapter is to critically assess the roles of global forest management in the global C cycle and mitigating climate change.

11.2 The Role of Forests in the Global Carbon Cycle

Global C cycling is presented in Fig. 6.1, and an excerpt representing conceptual global forest C cycling is presented in Fig. 11.1. Forests hold C stocks in living and dead biomass, where living trees capture and release C through photosynthesis and respiration, dead biomass decay and release C, and a fraction of this C eventually ends up in soils. Using energy from the sun and water from the soil, trees and the understory continuously cycle C through photosynthesis, growth, respiration, death, and decay. Photosynthesis convert CO_2 from the atmosphere into photosynthetic products [i.e., sugars, water, and oxygen (O_2)], which are used directly for cellular respiration and root exudation, or stored as more complex molecules as an energy store or for growth of leaves, stem, and roots. Overall, photosynthesis generally exceeds respiration, making most terrestrial ecosystems net sinks of C in natural state. When the tree growth is directed towards woody tissues—stems, branches, and large roots, it is referred to as biomass accumulation. Contrary to old accepted theory that old unharvested forests are in equilibrium in terms of C sink, new observations have shown that unharvested old forests are absorbing more C than they release (Luyssaert et al. 2008), accounting for the half of the terrestrial C sinks estimated at 3.0 ± 0.8 Pg C yr^{-1} for 2005–2014 period (Ciais et al. 2013). The C sink of the mature forests is attributed to large-scale environmental changes such as higher atmospheric CO_2 concentration and N emitted from agriculture and fossil

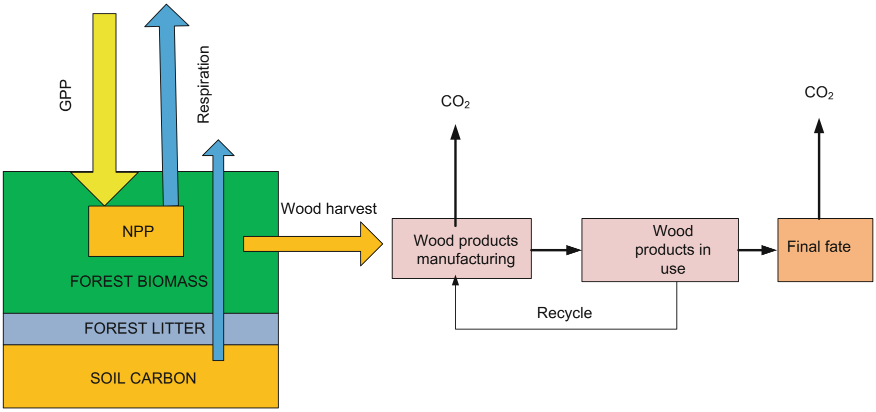

Fig. 11.1 Conceptual diagram of forest carbon cycle showing forest ecosystem and forest product use

fuel burning and deposited hundreds of kilometers away which is increasingly fertilizing forests in Europe, China and eastern USA (Solberg et al. 2009), causing violation of the steady-state conditions.

The mass of tree is composed nearly 50% C on dry mass, and natural systems dominate global C cycle. Terrestrial vegetation alone takes up an estimated 123 Pg C yr^{-1} and respiring 119 Pg C yr^{-1} (Ciais et al. 2013), which is about 13 times more than anthropogenic emissions from fossil fuels and cement production estimated at 9.3 ± 0.5 Pg C yr^{-1} for 2006–2015 decade (Le Quéré et al. 2015, 2016). These fluxes are dominated by forests, and the significance of forests to global C cycle is demonstrated by intra-annual variation of atmospheric CO_2 concentration which is expressed in sawtooth effect showing atmospheric CO_2 concentration that corresponds to the growing season in the northern hemisphere where most of land and forests exist (Fig. 6.2; Keeling 1960). For example, during northern hemisphere summers, photosynthesis exceeds respiration globally, and atmospheric CO_2 declines, whereas during northern hemisphere winters, respiration exceeds photosynthesis and atmospheric CO_2 concentration increases (Fig. 6.2). Forests contain 77% of all terrestrial aboveground C (Houghton 2007).

Because of forests, atmospheric CO_2 concentrations are not rising as rapidly as they would be predicted by adding anthropogenic CO_2 emissions to current levels in the atmosphere. Oceans are also absorbing additional 2.6 ± 0.5 Pg C yr^{-1} during 2006–2015 decade or 2.4 ± 0.5 Pg C since 1990 (Le Quéré et al. 2015, 2016). This phenomenon has been called a "loan from nature" and also a "buffer to climate change" (Philips and Lewis 2014). Tropical forests are the largest, most dense, and most diverse on Earth, but the high levels of deforestation within the tropics account for nearly all net forest loss and GHG emissions from forest land use across the planet. It is estimated that every year 72 Pg C cycle through tropical forests and savannahs, representing 59% of terrestrial GPP, the total influx of C from the atmosphere to plants per unit time (Beer et al. 2010). In addition to capturing C, forests also have vital interactions with climate, hydrological cycle, and nutrient cycle.

11.3 Estimation of Global Forest Area Trends and Its Carbon Pools

Climate change is predicted to create substantial shift in tree species distribution and forest structure (Gustafson et al. 2010) and these shifts require monitoring to understand how global forest resources are changing is important since global forests drive policy and resource flows at global, regional, and national levels. Assessing global forest resources and patterns of forest productivity is important for both scientific and practical purposes. For example, forest losses due to long-term land use change, especially land clearing in the tropics are important part of GHG emissions (Settele et al. 2014). Forest resources data are generally used for various purposes including estimation of global emission from land use and land use change, as well as climate change modeling (Petrescu et al. 2012; Smith et al. 2014). Such an assessment is necessary for the global C cycle studies as well as producing useful information required for planning and sustainable management of forest resources both on local and on regional scale (Corona and Marchetti 2007). The necessity of monitoring and quantifying the amount of C accumulated within forests has increased in view of mitigation of climate change efforts such as REDD + mechanisms. However, Estimates of GHG emissions from deforestation require information on both the area of forest loss and the corresponding C stock of the land that is cleared (Houghton 2005; Gibbs et al. 2007), which has remained a challenge to accurately quantify, especially tropical deforestation and associated C losses (Ramankutty et al. 2007). Knowledge of the structure, distribution and biomass of the global forests is advancing rapidly due to improved global observation systems and analysis techniques (Saatchi et al. 2011; Asner et al. 2012). Satellite systems, airborne observation systems, improved land-based inventory systems and ecosystem models are providing high resolution maps (Running et al. 2009; Shugart et al. 2010; Masek et al. 2015). Estimates of global area under forest and global forest C pools are generally obtained from different sources of information including: (i) field inventories, (ii) country reports, (iii) book keeping models, (iv) remote sensing, and (v) modeling.

11.3.1 Field Inventories

Field inventories are based on field sampling, and this approach has been used for more than a century, mainly for assessing timber supply and monitoring forest changes. It can be a foundation of forest C monitoring as an initial assessment of C stocks under forest from which changes can be estimated either using remote sensing or modeling and also as a direct estimate of stock change from repeated inventories. One of the main aspects of forest C pool—forest biomass has traditionally been measured and monitored with field inventory method which was developed for timber supply assessment (Birdsey and Heath 2001). Inventories are particularly suitable for monitoring vital elements of forest dynamics such as growth, harvest, and mortality, and also for estimating biomass, and when combined with remote sensing it can provide a quantifiable error estimate about forest inventory.

Forest inventory involves systematic or random selection of sampling locations in large areas—as large as countries, field measurements of tree parameters such as species, diameter, and height and the development of allometric equations estimating forest variables of interest that is difficult to directly measure—such as timber volume or biomass (Pearson et al. 2007; Birdsey et al. 2013). The inventory sampling approach provides unbiased estimates with known sampling uncertainty, even though uncertainty attributed to use of allometric equations or models is infrequently estimated (Phillips et al. 2000). Monte Carlo estimation methods can be used for estimating overall national uncertainty (Heath et al. 2011). Most of global forest statistics on forest biomass and other forest attributes reported by FAO are based on forest inventories obtained at national level (FAO 2010, 2015). Global estimate of forest area and biomass for the last two decades based primarily on ground data are based on comprehensive statistics obtained from the inventory approach (Pan et al. 2011). National inventories are often targeted to assess the population of live and dead trees in forest, while other ecosystem C pools can be estimated directly using supplemental measurements added to the inventory or modeled using exogenous data (Woodall et al. 2012).

Typically, biomass equations are developed for population of trees by harvesting and weighing a small sample of trees across a range of diameter and height classes and then estimating parameters of equation relating biomass to measured variables using regression techniques (Birdsey et al. 2013). Individual tree estimates can be expanded to tree population if the probability of sampling each tree and area to which sample apply is known. Also a variation of this approach has been used (FAO 2014).

Limitation of this approach include: (1) Scarcity of representative biomass or volume equations, since only few equations are available that represent the population of trees that may be different from the population of interest (Zianis et al. 2005). This is particularly true for tropical regions where such work is generally lacking (Brown 1997). Regression equations using three independent variables—tree diameter, tree height, and wood specific gravity can be used to reduce biases in such cases where equations are lacking (Chave et al. 2005). (2) Estimating the change in biomass of live trees requires successive measurements of sample plots at an interval of several years to estimate average rate of change in tree diameter and height. Inventory estimates from USA suggests that the largest C pools is in the live biomass and soils and contributes the most to overall estimates of forest C stocks and stock changes (Heath and Smith 2000), and overall uncertainty of estimated changes in forest C stocks for USA is ~21% (EPA 2015).

11.3.2 Country Reports

Country reports, often based on national forest inventories have generally been used for compilation of regional and global forest statistics. Food and Agriculture Organization of the United Nations (FAO) in their forest resources assessment reports and also Intergovernmental Panel on Climate Change (IPCC) have relied on country reports (FAO 2010, 2015; Ciais et al. 2013). Centralizing forest statistical information through country participation makes available the national statistics which have been used in number of scientific applications (Houghton 2005; Kindermann et al. 2008). Limitation of FAO forest resource assessment include lack of internal consistence due to different definition of forest among countries and also time intervals (Grainger 2008). Country reports sometimes provide incomplete data, especially from developing countries where resources are limited. FAO compiles two types of datasets—Forest Resources Assessment at 5-year interval which provides details about forest alone, while FAOSTAT datasets are more robust, and including estimates of emissions from different land uses as well as areas under croplands, pastures forests and other lands which is also useful for estimating land use and land use changes (FAOSTAT 2016).

11.3.3 Bookkeeping Model

The book keeping model uses data on rate of land use change and per hectare change in C storage that result from changes in land use and land management (Houghton 2003, 2005). Land use change includes clearing of land for cultivation and pasture, the abandonment of agriculture land, the harvest of wood, reforestation, afforestation, shifting cultivation, and wild fires. The book keeping model tracks C in living vegetation, dead plant material, wood products removal, and soils for each unit land area harvested or reforested. Rates of land use change are generally obtained from agriculture and forest statistics, historical accounts and country reports (Houghton 2003). This approach comprises of compiling information about changes in forest area from nationally aggregated land use statistics, satellite data on land cover and satellite data on wild fires and vegetation response curves to define per hectare changes in C density as a result of land management (Houghton et al. 2012). The bookkeeping model sums the observed changes in management. The global bookkeeping estimates are good approximation of area and C changes resulting directly from human activities.

11.3.4 Remote Sensing

Aerial photographs have been used for nearly a century in forest inventories to estimate the proportion of land under forest in a given sampling area and as a first phase sample in a double sampling strategy. However, in recent decades, the Landsat satellites have provided a time series of remotely sensed digital images that are widely used for establishing historical baselines and also for monitoring current deforestation, forest degradation and natural disturbances (Tran et al. 2016; Cohen and Goward 2004; Chen et al. 2016). Landsat imagery does not directly estimate biomass, however, but spectral attributes are related to biomass and can be used together with field data and models to provide spatially explicit biomass and other vegetation attributes over large areas (Cohen et al. 1996; Masek et al. 2015). When associated with field observations or models, Landsat satellites can also be used for estimating changes in biomass and C stocks. The series of remote sensed digital images span the last 30 year period and currently widely used for monitoring biomass and C stocks. Landsat data are suitable for classifying vegetation and assessing other attributes of forest such as percent forest cover, leaf area index, and disturbances (Cohen and Goward 2004; Tran et al. 2016; Chen et al. 2016). The

Moderate Resolution Imaging Spectroradiometer (MODIS) satellite also provides useful information about forest biomass, productivity and disturbances over large regions at a course spatial resolution (Running et al. 2004; Wang and D'Sa 2010; Rossi et al. 2013).

Three-dimensional remote sensing allows researchers to estimate forest canopy height, map the global forests, as well as estimating forest biomass and C stocks (Lefsky 2010; Ni et al. 2015). Many other ecological parameters such as forest succession and vegetation interactions are also assessed by three dimensional remote sensing. New tools are also providing decision support for forest management and ecological restoration. Remote sensing approaches are typically used to assess land cover and land cover change. They are not suitable for detecting land use or land use change, since it is usually difficult to separate human and natural causes of observed changes using remote sensing images without combining images with other information such as field inventory. It is also difficult to determine whether observed changes in land cover are permanent or temporary without an associated change in land use such as forest clear-cutting harvest. In general, remote sensing is combined with field sampling in national forest inventories to be more effective in identifying causes of change and improve overall monitoring efficiency.

11.3.5 Models

Varieties of ecosystem models have been used to quantify biomass and forest C dynamics through integration as well as synthesis of data covering different spatial and temporal scales ranging from detailed plot level measurement to national remote sensing products (Kurz et al. 2009; Wulder et al. 2008). Models also enable understanding of mechanisms controlling C exchanges between land and atmosphere, identify gaps in information, and guide future research to fill these gaps (Huntzinger et al. 2012). Models are also effective tools for predicting the future and comparing different scenarios to examine effects of different activities such as management or disturbance that have not been observed (Kurz et al. 2009). Available models can be grouped into process-based and empirical models. Process-based models uses information collected from intensive monitoring site such as leaf area index, soil conditions and climate variability to simulate C dynamics driven by photosynthesis processes (Running and Coughlan 1988). Bottom-up studies using dynamic global vegetation models (DGVMs) can mechanistically represent many of the key land processes and investigate how changes in the structure and function of the land ecosystems affect biogeochemical cycles and provide comprehensive analysis of surface C and mechanisms behind regional trends in C cycles (Sitch et al. 2015). Empirical models uses information derived from inventories and management plans such as wood volume yield data (Kurz et al. 2009; Masera et al. 2003).

11.4 Forest Area, Status and Trends

Global forests are increasingly affected by land use change, land fragmentation, changing forest management objectives, and degradation. Despite these factors, since 1990 the biomass in forest has consistently increased in global forests, suggesting that global drivers of elevated CO_2 may be enhancing biomass gains (Pan et al. 2013). In addition, all forests are responding to changes in atmospheric composition, especially increased NO_x and N deposition, increasing CO_2 concentration, and climate change. Sustainability of the future forests and the associated services provided by forests such as timber production, watershed protection, biodiversity, and the role of forests in removing anthropogenic CO_2 emissions depend on response of the global forests to these concurrent factors. Currently, the global C sink in established forest is estimated at 28% of anthropogenic CO_2 emissions (Pan et al. 2011; Le Quéré et al. 2015, 2016), and if this sink is reduced, the global efforts to mitigate climate change will require even further emissions reductions than currently projected (IPCC 2014). According to FAO, forest is defined as land with tree crown cover or stocking level of more than 10% and an area of more than 0.5 hectare (ha), with trees able to reach a minimum of 5 m at maturity in situ (FAO 2015). It may consist of closed forest formations with various open continuous forest vegetation cover in which tree crown exceeds 10% or various storeys and undergrowth cover with high proportion of ground. Young natural stands and plantations established for forest purposes which have not yet reached a crown density of 10% or tree height of 5 m as a result of human intervention causes such as clear-cutting are included under forest because these areas are expected to revert to forest. However, land that is predominantly agricultural or urban is not included, even if such land has some tree cover which meets the forest definition. The global land under tree cover can be classified into primary forest, protected forest, unmanaged natural forest, managed forest, plantation forest, and other wooded land (Table 11.1; FAO 2010, 2015). Although not technically considered as forest based on standard forest definition, trees outside forests are valuable source of many products and services found in forest.

Based on FAO estimate, the global forests currently covers about 3999 Mha of Earth's land surface equivalent to 31% of global land area in year 2015, distributed among all six continents (Table 11.2; FAO 2015). Tropical, sub-tropical, temperate, and boreal forests account for 44.3, 8.0, 17.1, and 30.6% of the area, respectively, (Table 11.3; Keenan et al. 2015). The bulk of global forest is natural (comprising the sum of primary forest and other naturally regenerated forest), amounting to 93% or 3700 Mha in 2015 (Table 11.4; FAO 2015). A further 1204 Mha are covered by other wooded land which does not fully meet the criteria for forest land distributed among tropical (43%), sub-tropical (33%), temperate (14%), and boreal (10%) regions (Table 11.3; Keenan et al. 2015). Europe (including the Russian Federation) has the largest forest area than any other region (25%), followed by South America (21%) and North and Central America. Three quarters of all forest is in high-income and upper middle-income countries, with about 25% of the total

Table 11.1 Forest land classifications

Class	Definition
Primary forest	Naturally regenerated forest of native species with no clearly visible indication of human activities and ecological processes are not significantly disturbed
Protected forest	Forest area within formally established protected areas regardless of the purpose for which the protected areas were established
Unmanaged natural forest	Forest land which is not under protected status and does not have a documented management plan. Some areas may be actively managed or may be direct human impacts such as forest harvesting
Managed natural forest	Forest area that has long-term documented management plans, aiming at defined management goals, which are revisited periodically. It excludes forest plantations and managed forests without documented plans
Plantation forest	Forests which are predominantly composed of trees established through planting and/or seeding. Plantation forests may be used for timber production or other purposes such as erosion control
Land outside forest with trees	
Other wooded land	Land not classified as forest, which can span form more than 0.5 ha with trees higher than 5 m and canopy cover of 5–10%, or trees able to reach these thresholds in situ, or with combined cover of shrubs, bushes, and trees above 10%. It does not include land under agricultural or urban land use
Agroforest	It is a collective name for land use systems and techniques where woody perennials—trees, shrubs, palms, bamboos, etc. are deliberately used in the same land management units as agricultural crops and/or animals in some form of spatial arrangement or temporal sequence (Lundgren and Rainee 1982)

Source FAO (2015)

Table 11.2 The trend in forest area from 1990 to 2015 by continents and sub-regions in each continent

Continent	Land area million hectare (Mha)					1990–2015 change (%)
	1990	2000	2005	2010	2015	
Africa	705.7	670.4	654.7	638.3	624.1	−11.6
Asia	568.1	565.9	580.9	589.4	593.4	4.4
Europe	994.3	1000.3	1004.1	1013.6	1015.5	2.1
North and Central America	752.5	748.6	748.0	750.3	750.7	−0.2
South America	930.8	890.8	868.6	852.1	842.0	−9.5
Oceania	176.8	177.6	176.5	172.0	173.5	−1.9
Total/world	4128.3	4053.6	4032.7	4015.7	3999.1	−3.1

Data source FAO (2015), Keenan et al. (2015)

forests in countries with economies classified as lower or middle income. Various natural and anthropogenic induced disturbances exert profound impacts on global forests. About 60% of the world's forest land area is recovering from the past disturbance and nearly 3% of the forest land is disturbed annually by logging, fire, pests, or weather related catastrophes such as drought. The FAO estimates of forest land area established from forest inventories and country reports differ from similar estimates based on remote sensing. For example, spatially explicit estimates of forest area based on remote sensed land cover indicated that FAO estimates based on land use are 94% of land cover based estimates (Erb et al. 2007). FAO has also used a satellite-based land cover approach to complement the inventory approach, and these independent results show slightly smaller global forest area that is 96% of the inventory approach (D'Annunzio et al. 2014). These differences are attributed to inherent contrasts in land use versus land cover indicators. Estimates based on tree cover may include land with trees that does not meet the inventory definition of forest because the observed tree cover may be below the percentage threshold used for classifying forest from inventory perspective or sometimes another land use that has significant tree cover such as commonly observed on urban or developed land. Land use indicators used in inventory estimates usually include land that are temporarily without trees such as recently harvested but not regenerated as forest land, whereas these areas can be classified as non-forest land type based satellite-based or remote sensed land cover because they lack observable tree cover.

Overall, the global forest area decreased by 3.1% between 1990 and 2015 (Table 11.2). Agriculture expansion has been the most important cause of recent forest loss, accounting for 80% of deforestation worldwide, and primarily during 1980s and 1990s through conversion of tropical forests (Gibbs et al. 2007; Houghton 2007). Climate change induced by anthropogenic GHG emissions is also becoming an important factor shaping forests globally (Walther 2010). Climate change triggers changes in disturbance regimes such as increased frequency and intensity of wild fires, windstorms, and insect outbreaks (Dale et al. 2001). In addition, altered rainfall patters and increased global temperature causes drought and heat stress around the world, resulting into increased tree mortality and sometimes forest die-off as well as decreased forest productivity as a result of interaction of multiple factors associated with the global climate change (Allen et al. 2010; Kurz et al. 2008; Phillips et al. 2009).

Although the total global area of forest land has declined, the category of planted forest has been increasing (Table 11.4). The area of protected forest has also increased, and management intensity of forest has increased significantly with substantial gains in the area under planted forests and forests with management plan (Keenan et al. 2015; FAO 2015). Consequently, the trends in unmanaged natural forest have been sharply declining (Table 11.4). Therefore, human-induced deforestation from 1990 to 2015 was partly offset by increases in forest area that has both natural regrowth after abandonment and human causes such as plantation forests. The net change in forest area is a result of net effect of forest clearance and conversion to other land uses (deforestation) and afforestation (where forest is planted or regenerates naturally on previously cleared land) and reforestation

Table 11.3 Trends in forest and other wooded land in different climatic domains between 1990 and 2015 (FAO 2015)

Climatic domain	Forest land area in million hectare (Mha)				
	1990	2000	2005	2010	2015
Forest area					
Boreal/polar	1219.3	1219.8	1218.9	1224.9	1224.5
Temperate	618.0	640.9	659.2	673.4	684.5
Tropical	325.4	324.8	323.9	319.6	320.1
Sub-tropical	1965.5	1870.1	1830.8	1797.8	1770.2
Total/world	4128.3	4055.6	4032.7	4015.7	3999.1
Other wooded land area					
Boreal/polar	121.2	117.7	119.6	122.0	121.2
Temperate	157.6	154.5	159.6	163.7	167.3
Tropical	150.1	149.1	151.4	150.6	399.1
Sub-tropical	549.0	533.1	523.1	537.8	516.9
Total/world	978.5	954.4	953.7	974.2	1204.5

(where trees are planted or regenerates naturally on lands classified as forest). The rate of net forest loss has halved over the 25-year period, falling from 7.3 Mha yr^{-1} in the 1990s to 3.3 Mha yr^{-1} between 2010 and 2015 (Table 11.2), although this reduction is not equivalent to the reduced rates of human-induced deforestation. Deforestation or forest conversion is more complicated than just forest area decrease, because globally, forest gain and losses occur continuously and new forests of different type and environmental benefits are generally created, which are much harder to monitor (FAO 2015). Natural forest change is a better indicator of natural habitat and biodiversity dynamics. The primary forest is defined as: “naturally regenerated forest of native species where there are no clearly visible indications of human activities and the ecological processes are not significantly disturbed” (Morales-Hidalgo et al. 2015). Their key characteristics include: showing natural forest dynamics, such as natural tree species composition, occurrence of dead wood, natural age structure, and natural regeneration processes; the area is large enough to maintain its natural characteristics; there has been no known significant human intervention or the last significant human intervention was long ago enough to have allowed the natural species composition and processes to have become re-established. Global primary forest area accounted for 35% in 2015 (FAO 2015). The global primary forest area declined by 6% between 1990 and 2015 (Table 11.4; Keenan et al. 2015), due to forest clearance followed by conversion to other land use (i.e., deforestation) in some areas, forest fire, or drought that has led to total deforestation. Fire is the most significant cause of forest loss in boreal forests (Potapov et al. 2008), while deforestation is the dominant cause of forests loss in the tropical ecozone (Hansen et al. 2013). The tropical dry forests of South America have the highest rate of tropical forest loss due to deforestation. The largest loss (11%) occurred in the tropics, while temperate regions gained natural forest, mainly from regeneration in Europe and Asia (Table 11.4; FAO 2015; Keenan et al. 2015). Primary forests are generally reclassified as other naturally regenerated forests after the disturbance. Overall, disturbances varying in type, scale, intensity, and frequency create complex mosaic of forest distribution globally and high landscape scale diversity, while also setting the initial conditions for dynamics and structural development (Swanson et al. 2011).

Natural forest generally describes forest vegetation that evolved naturally in an area, while plantation forest includes intensively managed forest plantations purposely established, commonly composed of single tree species, established to give priority to wood production. Conversion of natural forest area into an intensively managed forest plantation of exotic tree species may increase timber production potential but will generally reduce its biodiversity and ecosystem services. Some plantation forests are also established for land conservation, coastal stabilization, biodiversity conservation or other purposes. Loss of natural forest in some parts are offset by afforestation and plantation forest elsewhere. Protective forest area remained fairly constant over the 25-year period with a mean of 35.9% of the total forest area. The main categories for the protective forest area in 2015 were clean water (3.5%), coastal stabilization (0.83%), desertification control (3.6%), avalanche control (3.1%), public recreation (4.5%), C storage (1.3%), cultural services (1.9%), and other services (2.0%) (Miura et al. 2015). The land area with trees outside forest has increased as the developed land and urban area have increased (Table 11.3; Guo et al. 2014). Also, some of formerly dry woodlands not satisfying the definition of forest have greened (Brandt et al. 2015; Piao et al. 2015).

In addition to both natural causes such as drought, natural fires, storms, and diseases and pests and also anthropogenic activities such as clearance for agriculture, changes in land use and land cover from forest to non-forest are also associated with over-exploitive timber harvesting, the expansion of settlements, and infrastructure development. Change of forest to other land uses are linked to a complex and multifaceted set of underlying driving forces including population growth, poverty, government policies, technological development, rural to urban migration, changes in cultural attitudes towards forests lack of stronger incentives for conservation.

11.5 Global Forest Biomass Accumulation and Productivity Trends

Plants fix CO_2 as organic compounds through photosynthesis, a C flux also known at the ecosystem level as gross primary production (GPP). The terrestrial GPP is the largest global C flux of the global C cycle in the terrestrial ecosystem, and it drives several ecosystem functions such as respiration and growth, while impacting all of the global C cycle (Beer et al. 2010). It also forms the basis for both human and animal food, and also fiber and wood production. In addition, GPP together with respiration is one of the major processes controlling land-atmosphere CO_2 exchange, and accurate quantification of GPP provides a sound scientific foundations for predicting future changes in atmospheric CO_2 through understanding C

Table 11.4 Natural forest area trends from 1990 to 2015 by climatic regions estimated based on total forest area and planted forest

Climatic domain	Forest land area in million hectare (Mha)					1990–2015 change (%)
	1990	2000	2005	2010	2015	
Natural forest						
Boreal/polar	1189.2	1179.0	1171.8	1170.5	1166.7	−1.9
Temperate	529.1	531.9	534.8	538.8	545.8	3.1
Tropical	307.1	303.7	301.3	295.5	295.2	−3.9
Sub-tropical	1935.2	1831.4	1785.7	1745.2	1713.3	−11.5
Total/world	3960.7	3846.0	3793.6	3750.0	3721.2	−6.0
Planted forest						
Boreal/polar	30.1	40.8	47.1	54.4	57.7	91.6
Temperate	88.9	109.0	124.4	134.6	138.7	56.1
Tropical	18.3	21.0	22.6	24.1	24.7	35.1
Sub-tropical	30.3	38.8	45.1	52.5	56.8	87.5
Total/world	167.6	209.6	239.2	265.7	278.0	65.9

Data from FAO (2015)

sources and sinks, while also defining the management options for the global C cycling (Yu et al. 2014). The global GPP is estimated at 122 Pg C yr^{-1}, and 49% of this occurs in forest (Beer et al. 2010), while other lands, including croplands, grasslands, and savannahs also have significant rates of GPP (Table 11.5). The global NPP is estimated to be approximately half of GPP (Table 11.5), but C use efficiency (CUE, i.e., the ratio of NPP to GPP) describes the capacity of forests to transfer C from the atmosphere to the tree biomass, and it varies among biomes (DeLucia et al. 2007).

On an annual basis, the tropics have the highest biomass accumulation, followed by temperate and the boreal (Table 11.5). Boreal forests have very high NPP in their growing season but the growing season is very short in boreal regions. Boreal forests occupy large areas of northern hemisphere, mainly found in Canada, Russia, Alaska and Scandinavian region. Biodiversity is generally low in boreal forests. It is estimated that boreal forests contain about 60–100 Mg C ha^{-1}, of which, about 80% is in the aboveground biomass (Luyssaert et al. 2007; Malhi et al. 1999). Decomposition of OM is generally slow due to low temperatures, and therefore, large accumulation of C exists in soil pool, estimated at 116–343 Mg C ha^{-1} (Malhi et al. 1999; Amundson 2001). Temperate forests are found in climate with distinct seasons—a well-defined winter and regular precipitation. The overall C store has been estimated to be between 150 and 320 Mg C ha^{-1}, of which, plant biomass in the form of large woody aboveground and deep coarse root system accounts for about 60% and the soil C is about 40% (Amundson 2001). The warm and wet tropical moist forests result in rapid plant growth and most of its C is found in the vegetation with biomass estimates of 150–250 Mg C ha^{-1} (Amundson 2001; Chave et al. 2008; Lewis et al. 2009b). On average, the tropical forests are estimated to store 160 Mg C ha^{-1} in the aboveground biomass, and about 40 Mg ha^{-1}

Table 11.5 Current global forest productivity and estimates of biomass productivity (Pan et al. 2013; Prentice et al. 2011)

Biome	GPP ($Pg\ C\ yr^{-1}$)	NPP ($Pg\ C\ yr^{-1}$)	Current biomass (Pg C)	Potential biomass (Pg C)	Existing C relative to potential (%)
Tropical forest	40.8	21.9	262.1	352.0	74
Temperate forest	9.9	8.1	46.6	161.0	29
Boreal forest	8.3	2.6	53.9	180.0	30
Subtotal major forest biomes	59	32.6	362.6	690.0	53
Other lands except cropland	47	25.9	10.8	79.0	14
Cropland	14.8	4.1	10.8	–	–
Total	121.6	62.6	393.4	772.0	51

belowground in roots. Soil C stocks are estimated at about 90 Mg C ha^{-1} and somewhat lower than biomass stock (Amundson 2001). Currently tropical forests are considered to be a C sinks with recent research indicating an annual global uptake of about 1.3 Pg C yr^{-1}, Central and South America is estimated to takes about 0.6 Pg C yr^{-1}, African forests about 0.4 Pg C yr^{-1}, and Asian forests about 0.25 Pg C yr^{-1} (Lewis et al. 2009a). Tropical forests account for two-thirds of all terrestrial biomass, while temperate and boreal forests are each equivalent to ~20% of tropical biomass. Globally, forests account for 92% of all biomass, and therefore, the distribution of forests is equivalent to the global distribution of biomass (Prentice et al. 2011).

Ice core records reveal that glacial periods were associated with lower atmospheric CO_2 concentrations (Siegenthaler et al. 2005; Luethi et al. 2008; Higgins et al. 2015). Although low CO_2 concentrations are not the cause of glaciations, the concentrations of 170–200 ppm were repeatedly reached during the glacial maxima. The last glacial maximum (LGM) from 26,500 to 19,000 years ago (Clark et al. 2009) is the cold glacial period with the most comprehensive paleodata. The atmospheric CO_2 concentration was also ~75 ppm lower than Holocene period. Studies from paleoecology and modeling suggest that the global C storage in vegetation and soils was smaller, with GPP and NPP estimated at approximately 86.3 and 41.0 Pg C yr^{-1}, respectively, and the global terrestrial aboveground biomass C of ~340 Pg C (Adams et al. 1990; Prentice et al. 2011). After the LGM, however, the global C storage almost doubled and peaked at ~770 Pg C during the pre-agricultural disturbance era ~10,000 years ago (Adams et al. 1990; Prentice et al. 2011). Based on global forest aggregation field observations, current aboveground forest biomass estimates are 470 Pg C (Table 11.7) and the global C of the forest living biomass is estimated at ~270 Pg C (Kohl et al. 2015), suggesting large potential for C sequestration in global biomass. Human utilization of biomass products is mostly responsible for the actual and potential biomass globally. It is estimated that currently humans are removing ~16.3 Pg C yr^{-1},

Table 11.6 Forest C pool and C density by forest biome (Pan et al. 2011, 2013)

Biome	Live biomass C (Pg C)	Soil organic C (Pg C)	Carbon density (Mg C ha^{-1})	
			Live biomass	Soil organic C
Boreal	53.9	217.6	47.5	191.7
Temperate	46.6	72.0	60.7	94.0
Tropical	228.2	165.1	163.9	118.6
Tropical regrowth	33.9	43.8	60.8	78.6
Global	362.6	498.8	94.1	129.4

approximately a quarter of the global NPP (Haberl et al. 2007) in the form of biomass products such as food, fiber, wood products and bioenergy. In addition, forest degradation which lowers biomass density has played significant role in reducing the capacity of forests to provide the needed goods and services globally. Human-caused reduction in forest biomass C varies across the biomes. For example, in the tropical zones forest biomass is 74%, while in boreal zones where forests occur naturally, the current biomass is only 30% of what the potential would be without human use of the land for food production, fiber, and other non-forest land uses (Table 11.5). Even as many countries in temperate zone are experiencing transitions from net deforestation to net reforestation in terms of land area, the land area under forest and also biomass C density still remain lower than that during the pre-agricultural state (Table 11.5).

Based on pre-agricultural biomass content in the global biomass, it is estimated that global forests currently contain about half of the biomass that would be present without human use of land for food, fiber, and other non-forest uses (Table 11.5; Prentice et al. 2011; Pan et al. 2013). However, how much of the potential increase in C stocks could be realized as the part of mitigation programs to offset the CO_2 increase will mostly depend on societal economic and social constraints. Increasingly, C stock are not the only management goal of forests or other lands. Nabuurs et al. (2007) conducted a comprehensive analysis and estimated that the global forests activities have mitigation potential to sequester an additional 3.8 Pg C yr^{-1} from afforestation, reduced deforestation, and improved forest management at a cost of $50 to 100 per ton of CO_2. About 1.6 Pg C yr^{-1} of the estimated 3.8 Pg C yr^{-1} could be achieved from reduced deforestation (Nabuurs et al. 2007). This will increase the gross C uptake by forests estimates from 4.0 Pg yr^{-1} (Pan et al. 2011) to about 6.2 Pg C yr^{-1}, a potentially maximum C sequestration by global forest ecosystems that can be expected.

The live biomass C store of the global forest was estimated by FAO in 2015 to be 296 Pg C in both above- and below-ground biomass, about half of total C stored in forests. The global average C density is estimated at 74 Mg ha^{-1}, with the highest densities in South America and Western and Central Africa storing 120 Mg C ha^{-1} in living biomass (FAO 2015). Pan et al. (2011, 2013) reported live biomass C stock densities for the tropical forests of 134 Mg C ha^{-1}, with an estimated tropical live biomass C of 248 Pg C (Table 11.6). In contrast, Saatchi et al. (2011) reported live biomass C stock densities for tropical forests of 100.5 Mg C ha^{-1}, similar to those repoted by FAO (2010, 2015), suggesting an overestimation for both tropical forest C stock density and biomass C by Pan et al. (2011, 2013). The FAO biomass C stock densities for tropical forests sub-regions rang around those of Saatchi et al (2011) estimate, with the highest being South America at 122.4 Mg C ha^{-1} and the lowest being Eastern and South Africa at 69.5 Mg C ha^{-1} (FAO 2010, 2015). Compared to 1990, the global biomass declined by 0.52% with largest decline occurring in subtropical forests (−8.3%). The temperate forests saw 27.1% increase in biomass relative to 1990 (Table 11.6). Although the global forest biomass has been fairly stable since 1990, the biome-specific changes reflects the status and trends of recent human use of biomass and the environmental factors in different regions of the Earth. The biomass of temperate forests is increasing, probably because of combination of factors that include continuing regrowth following abandonment from agricultural land, logging, and environmental factors such as N deposition, increasing atmospheric CO_2 concentration and changing climate (Pan et al. 2011). Timber production has remained relatively stable since 1990, although areas of forest used for non-wood forest products indicate that harvesting is taking place on smaller proportion of total forest area while harvesting for biofuel has increased in recent days. The indirect effect of concentrating timber production on a smaller land base and establishment of plantation forests is to reduce harvesting on other forest areas where C stocks may increase in the absence of harvest. However, these areas are subject to higher C losses from natural disturbances including drought, as evidenced in Western USA and other areas (Allen et al. 2010; Hicke et al. 2012).

11.5.1 Emission Trends and Drivers

Estimating anthropogenic component of gross and net forest land use emissions is difficult compared to other sectors since (i) it is not always possible to separate anthropogenic and natural GHG fluxes from forest land, (ii) the input necessary to estimate GHG emission globally and regionally often based on country level statistics or on remote sensing information are highly uncertain, (iii) methods for estimating GHG emissions uses a range of approaches from simple default methodologies such as the IPCC guidelines (IPCC 2006) to more complex estimates based on the terrestrial C cycle modeling and/or remote sensing information.

Fluxes resulting directly from forest land use activities are dominated by CO_2, primarily emissions from deforestation, but also an uptake due to reforestation/regrowth. Non-CO_2 GHG emissions from forest land use are small and mainly arise from peat degradation through drainage and biomass fires. Estimated land use change emissions from 1750 to 2014 are 190 ± 65 Pg C, about 31% of anthropogenic CO_2 emission, and 10% of anthropogenic CO_2 emission in 2004–2015 (Houghton et al. 2012; Le Quéré et al. 2015, 2016). The declining fraction is largely the result of the increasing fossil fuel emissions and also declining emission from land use change. The net flux of CO_2 from the land use change is also the most uncertain term in the C budget, accounting for emissions of 1.4 ± 0.5 Pg C yr^{-1} in 1980s, 1.6 ± 0.5 Pg C yr^{-1} in 1990s, and 1.1 ± 0.5 Pg C yr^{-1} in 2000s (Houghton et al. 2012; Le Quéré et al. 2015). The terrestrial land C sink from 1750 to 2015, mostly as a result of forest uptake, estimated as a residual C after accounting for atmospheric CO_2 concentration increase and ocean sink, is 165 ± 70 Pg C (Le Quéré et al. 2015, 2016), suggesting a net emission of ~25 Pg C from land use change during the Industrial Era.

Human-induced global environmental changes exert complex effects on forest productivity and C storage (Friedlingstein et al. 2006). Some of the factors driving the environmental changes are direct and physically alter forest areas and structures —such as tropical deforestation which destroy vegetation structures and habitat, and immediately releases large amounts of C stored in biomass as CO_2. However, some factors operate through tree physiology and ecological processes—such as changes in climate (temperature, precipitation, radiation) and atmospheric composition (e.g., CO_2 concentration, N deposition, O_3), and other pollutants (Boisvenue and Running 2006; Lewis et al. 2009a). Further, these factors may interact (i.e., drought induced forest diebacks, changes in forest structure and morphology) and interfere with C metabolism and dynamics (Walther 2010). The average global land use emissions from 2000 to 2015 are estimated at 1.0 ± 0.5 Pg C yr^{-1}, which is lower than 1990s emissions estimated at 1.6 ± 0.7 Pg C yr^{-1} (Friedlingstein et al. 2010; Le Quéré et al. 2015, 2016).

Global forest land use CO_2 fluxes estimates are based on wide range of data sources and includes different processes, definitions, and approaches to calculating emissions. These include CO_2 fluxes from deforestation, afforestation, forest degradation and harvesting activities (logging), regrowth of forests following wood harvest or abandonment of agriculture. Some of these managements lead to emission of CO_2 to the atmosphere, while others leads to CO_2 sinks. Deforestation and forest degradation, primarily in tropical regions accounted for 12–20% of global anthropogenic GHG emissions in 1990s and early 2000s (van der Werf et al. 2009). It is also expected that deforestation and forest degradation in the tropics will have the major impact for the future potential of forests to sequester the additional anthropogenic CO_2 emissions (Chave et al. 2008; Lewis et al. 2009b; Field et al. 1998). Over the period 1750–2014, forest was a net source of CO_2 and the land as a whole was a net sink of CO_2 since 1950s as confirmed by inventory measurements in managed forests in temperate and tropical regions (Phillips et al. 1998; Luyssaert et al. 2008; Pan et al. 2011). A sink is due to indirect effects of human activity on ecosystems, i.e., environmental change effects such as the fertilizing effects of increased levels of CO_2 and N in the atmosphere and the effects of on C storage (Le Quéré et al. 2009; Canadell et al. 2007a). However, some of it may be due to direct forest management change activities and not accounted for in the current estimates (Erb et al. 2013). A substantial fraction of current C sink is currently incorrectly attributed to environmental change, when it is a result of changes in management practices (Erb et al. 2013). This sink capacity is relevant to forest mitigation through forest protection. There has been a decline in forest land use emissions over the most recent years largely due to a decrease in the rate of deforestation (FAO 2015; FAOSTAT 2016). Forest land use emissions peaked in the 1980s in Asia and Latin America regions and declined thereafter, consistent with reduced rate of deforestation, notably in Brazil and some areas of afforestation in China, Vietnam, and India (FAOSTAT 2016). In the Middle East and Africa, the bookkeeping model showed continuing emissions from 1970 to 2000 (Houghton et al. 2012), while models show continuing increase from 1970 to 2000 and a small sink in the 2000s (Kato et al. 2013). The general picture in temperate and boreal regions is of declining emissions and/or increasing sinks. The temperate regions include a large areas of managed forests subjected to harvest and regrowth and areas of reforestation e.g., following cropland abandonment in USA and Europe.

The bookkeeping estimate (Houghton 2003, 2012) uses regional biomass growth and decay rates from the country inventories that are generally not adjusted for changes in climate or CO_2 concentration (i.e. CO_2 fertilization). It takes into account the forest management associated with shifting cultivation in tropical forest regions and also global wood harvest and regrowth cycles. The primary source of data for bookkeeping model is FAO forest area data and wood harvest (FAO 2015). The quality and reliability of the country inventory data varies considerably because not all countries have well-established forest inventory and monitoring programs. The FAO estimate of CO_2 emission with reference to 2001–2010 decade indicated that forest emissions were 0.9 Pg C yr^{-1}, of which, deforestation was 1.04 Pg C yr^{-1}, forest degradation and management was −0.5 Pg C yr^{-1}, biomass fires emissions were 0.1 Pg C yr^{-1} and drained peatlands contributed 0.25 Pg C yr^{-1} (FAOSTAT 2016). The FAO estimated that decadal net forest emissions decreased from 1.1 Pg C yr^{-1} in 1991–2000 to 0.9 Pg C yr^{-1} in 2001–2010 (FAOSTAT 2016). Using forest inventory data and long-term C studies, Pan et al. (2011) estimated a total global forest C sink of 2.4 ± 0.4 Pg C yr^{-1} for 1990–2007. The emission source from tropical land use change was also estimated at 1.3 ± 0.7 Pg C yr^{-1} of which tropical deforestation emissions of 2.9 ± 0.5 Pg C yr^{-1} is partially offset by C forest regrowth of 1.6 ± 0.5 Pg C yr^{-1} (Pan et al. 2011). The global forest C fluxes therefore, comprised of a net global sink of 1.1 ± 0.8 Pg C yr^{-1}, however, tropical estimates have the highest uncertainties. The FAO global forest resources assessment data show that the growing forest biomass volume has increased in East Asia, western and Central Asia, North America, Europe, Caribbean, and Oceania, while Africa and South America observed significant decrease in C pools between 1990 and 2015 (Table 11.7, FAO 2015). Overall, FAO reported decrease in global forest C pools between 1990 and 2015 (Table 11.8), mainly driven by decrease in South America and Africa.

Table 11.7 Biomass trends in the global forest of the major biomes (FAO 2015)

Biome	Year					Change 1990 and 2015 (%)
	1990	2000	2005	2010	2015	
Aboveground biomass in living forest (Pg)						
Boreal	78.17	77.80	77.66	77.97	78.45	0.35
Temperate	47.53	52.90	55.69	58.86	60.40	27.07
Subtropical	27.30	27.58	27.50	27.93	25.02	−8.33
Tropical	317.65	321.71	314.45	308.21	304.35	−4.19
Global total	470.65	479.99	475.30	472.97	468.22	−0.52
Belowground biomass in living forest (Pg)						
Boreal	19.52	19.55	19.52	19.66	19.88	
Temperate	11.01	12.30	12.97	13.97	14.13	
Subtropical	9.15	9.20	9.23	9.28	8.50	
Tropical	77.58	78.01	76.15	74.43	73.17	
Global total	117.27	119.06	117.87	117.11	115.68	

Table 11.8 Estimated forest carbon pools in different biome and year (FAO 2015; Pan et al. 2011, 2013)

Biome	Year					Change 1990 and 2015
	1990	2000	2005	2010	2015	
Boreal						
Aboveground	39.09	38.90	38.83	38.99	39.22	
Belowground	9.76	9.78	9.76	9.83	9.94	
Live biomass	48.85	48.67	48.59	48.82	49.16	0.65
Deadwood and litter	34.30	34.06	34.20	34.54	34.64	0.99
Soil	103.55	103.06	103.20	103.69	103.71	0.15
Temperate						
Aboveground	23.34	25.97	27.32	28.87	29.62	
Belowground	5.38	6.01	6.33	6.70	7.19	
Live biomass	28.73	31.98	33.65	35.55	36.50	27.05
Deadwood and litter	9.09	9.44	9.64	9.96	9.93	9.25
Soil	25.20	25.12	25.38	27.12	24.27	−3.70
Sub-tropical						
Aboveground	13.36	13.54	13.51	13.72	12.29	
Belowground	4.52	4.58	4.59	4.59	4.23	
Live biomass	17.83	18.07	18.15	18.26	16.28	−7.61
Deadwood and litter	1.52	1.54	1.55	1.56	1.57	3.09
Soil	6.73	6.73	6.70	7.27	7.25	7.82
Topical						
Aboveground	154.45	156.17	152.71	149.71	136.83	
Belowground	37.45	37.62	36.73	35.92	32.64	

(continued)

Table 11.8 (continued)

Biome	Year					Change 1990 and 2015
	1990	2000	2005	2010	2015	
Live biomass	191.92	193.93	189.72	185.85	168.12	−12.40
Deadwood and litter	7.47	7.16	6.98	6.93	6.44	−13.80
Soil	73.48	70.78	69.31	68.20	59.57	−18.94
Global total						
Aboveground	230.24	234.57	232.37	231.29	217.96	
Belowground	57.12	57.98	57.42	57.06	54.01	
Live biomass	287.33	292.67	290.12	288.48	270.26	−5.94
Deadwood and litter	52.38	52.19	52.37	52.99	52.58	0.38
Soil	208.97	206.26	205.07	206.28	194.81	−6.78
Total forest C	548.68	551.12	547.56	547.75	517.65	−5.66

11.6 Climate Change Mitigation Options Under Forest

Forests and climate change are intrinsically linked beyond C sequestration. Climate change and global warming could change forest landscape worldwide. Higher mean annual global temperatures, altered precipitation patterns, and more frequent extreme weather events may have adverse effects on forests, including stress, compositional and fractional changes and changes in the capacity of forests to provide products and services, and these effects are poorly understood. Since forest ecosystems capture and store CO_2 and make major contribution in the mitigation of climate change, when forests are destroyed through over-harvesting or burning they become a major source of CO_2 emissions. Conversion of forests to agricultural land also leads to the loss of soil organic C (SOC). The largest loss in SOC stock was reported when temperate (52%) followed by tropical forests (41%) and boreal forests (31%) were cleared (Wei et al. 2014). Due to the observed large losses of SOC resulting from conversion of forests to agricultural land, C storage capacity of the land will be increased through afforestation or decreasing deforestation (Poeplau et al. 2011; Wei et al. 2014). Afforestation of temperate croplands creates C sink of about 116% higher than cropland for the period of 100 years, and no new equilibrium was reached within 120 years (Poeplau et al. 2011).

Concerns about the role of forests in global climate have led to creation of collaborative mechanism for reducing emissions from deforestation and forest degradation under the United Nations Framework Convention on Climate Change (UNFCCC) with the goal of significantly reducing emissions from deforestation and forest degradation (REDD+) global partnership and collaboration (UN-REDD 2010). The UNFCCC has outlined two major goals with respect to forests: (i) using forests for biological C capture and storage, thus reducing the emissions of GHGs, and therefore, forests becomes part of mitigation strategy for climate change, (ii) using forests and tree biomass as part of strategy to cope with impacts of climate change, therefore forests become part of a climate strategy for adaptation (Van Bodegom et al. 2009). Forest-based climate change mitigation measures are low-cost and effective in short to medium term. Mitigation activities in forest can reduce climate forcing through: (i) conservation of existing C pools in forest (i.e., conservation of forest biomass, peatlands and soil C that could otherwise be mineralized, (ii) reduction of C losses from biota and soils through management changes within the same land use type (e.g., reducing deforestation, recreating wetlands and peat lands), (iii) enhancement of soil C sequestration, increasing C uptake by biota and long-lived products through tree planting—reforestation and/or afforestation, (iv) increasing C storage per unit area such as increasing stocking density in forests and wood use in construction, (v) changes in albedo resulting from land cover change that result in increased reflection of visible light, and (vi) use of forest products to replace high emission products such as replacing concrete and steel in construction with wood and also use of forest byproducts for bioenergy to replace fossil fuels. Summarized mitigation options associated with forest land use are presented in Table 11.9.

Summary of option for mitigation under forests are presented in Table 11.9. Forest ecosystems contain up to 80% of all aboveground terrestrial C (Dixon et al. 1994). Forests stores vast pools of C globally and even small shifts in the balance between photosynthesis and ecosystem respiration result in a large change in the uptake or emission of CO_2 from forests to the atmosphere. Processes that increase terrestrial C sequestration include land and soil management practices that enhance the storage of C, or reduce CO_2 emissions. Photosynthesis process can be enhanced by the processes that deliberately augment natural C uptake in plants. The rate of net CO_2 uptake by forests varies in a predictable way as forests grow from establishment or recover from the past disturbances (Pregitzer and Euskirchen 2004). Productivity in forest is generally a function of light and N supply (Hardiman et al. 2013). Investigations of forest NPP over the course of ecological succession support a general trend of declining production with forest age, but with knowledge gaps for late successional, mixed forests (Gough et al. 2008). Quantitative syntheses reports lower NPP in old-growth rather than young aggrading forests (Pregitzer and Euskirchen 2004; Luyssaert et al. 2008). Understanding factors that influence the rate of CO_2 uptake by vegetation is the basis for improving the forest management (Birdsey et al. 2006).

Forest C storage can be increased by planting of new forests on previously unforested lands (i.e., afforestation) or on previously forested lands (i.e., reforestation, for example, on lands that were previously cleared for agriculture) (Sochacki et al. 2012; Bustamante et al. 2014). This can include mixed species or monocultures. Afforestation and reforestation also provides social, economic, and other environmental benefits. Forest restoration in the degraded forests and protecting secondary forests with low C densities while allowing them to sequester C either by natural or artificial regeneration and long term fallows will also increase C sequestration in forest (Reyer et al. 2009). Other activities that promote C storage in forests include improved forest management and reducing deforestation or deforestation avoidance (van Bodegom et al. 2009). Improved management to enhance

Table 11.9 Summary of forest land use greenhouse gases and climate change mitigation strategies

Category	Practices	Reference
Reducing deforestation	Conservation of existing C pools in forest vegetation and soil by controlling deforestation, protection of forest reserves and controlling/minimizing other anthropogenic disturbances such as fires and pest outbreak. Reducing slash and burn agriculture, reducing forest fires. Protection of peatland forests, reduction of wild fires	Van Bodegom et al. (2009), Thorburn (2013)
Afforestation	Improved biomass by planting trees on non-forested agricultural lands. This includes both monoculture and mixed species planting	Sochacki et al. (2012), Bustamante et al. (2014)
Reforestation	Restoration of forests to the lands originally under forest but forests were lost by either natural or anthropogenic land degradation	Bustamante et al. (2014)
Forest management	Management of forests for sustainable timber production including extending rotation cycles, reducing damage to remaining trees, reducing logging waste, implementing soil conservation practices, forest fertilization, and using wood judiciously and more efficient way, sustainable extortion of wood energy. Wild fire control and behavior modification	DeFries and Rosenzweig (2010)
Forest restoration	Protecting secondary and tertiary forests and other degraded forest whose biomass and soil C densities are less than their maximum value and allowing them to sequester more C by natural or artificial regeneration and rehabilitation of degraded lands, long-term fallows. Wildlife behavior modification	Reyer et al. (2009)
Agroforestry, agropastoral and agrosilvopastoral systems	Mixed production systems increases productivity and efficiency in water and other resources and also protect against soil erosion as well as serve the C sequestration objective	Luedeling and Neufeldt (2012), Sinare and Gordon (2015)

productivity, controlling diseases and fire management during the forest lifecycle, extending rotation cycles, and reducing logging waste also increases C sequestration (DeFries and Rosenzweig 2010). Protecting forests form wild fires increases C stocks. However, with climate change effects, it may also increase a risk of larger releases of stored C (Westerling et al. 2006). Afforestation of abandoned agricultural land and degraded land generally increases soil C in addition to producing wood biomass (Guo and Gifford 2002). Avoiding deforestation and forest degradation preserves existing C stock that would otherwise be lost to the atmosphere. C storage in managed forests can also be enhanced by timber harvest and tree planting practices that increase C density (i.e., OC per unit area) and reduce forest degradation. The C sequestration can also be enhanced through management of forest stands on farms (agroforestry) and in urban and suburban settings (urban forestry). However, full accounting for different management action requires knowledge of changes in ecosystem C pools (Echeverria et al. 2004), harvesting wood products (Schlamadinger and Marland 1996) and fossil fuel emission associated with growing harvesting, and manufacturing (Schlamadinger et al. 1997).

One of the climate mitigation potential of forest which has not received enough attention is the biophysical effects of land management on climate which goes beyond C storage to account for surface albedo and evapotranspiration which have direct effects on climate. Some aspects of this have been evaluated with respect to land use change. However, Luyssaert et al. (2014) noted that biophysical changes within land class may have an effect of similar magnitude to that of changes in land class.

11.7 Conclusions

Forests, climate, climate change, and climate change mitigation are intricately linked. Forests cycle large amounts of C and, with proper management they could be utilized to remove anthropogenic CO_2 emissions from the atmosphere. Annual land CO_2 fluxes are dominated by forests, and it could become a large source of CO_2 emissions or substantial part of the mitigation depending on how they are treated internationally and managed locally. Terrestrial ecosystems, dominantly forests, have so far played an important role in controlling the increase in atmospheric CO_2 concentrations by removing about one third of the anthropogenic CO_2 emissions each year. However, the historical consequence of increasing intensity of global land management has been the long-term reduction of terrestrial C stocks as land has been converted to crops, pasture, and settlement for human life support. As a result, climate mitigation policies of potential to increase C stocks on lands with lower C stocks than expected compared with lands such as highly stocked old growth forests that have experienced relatively less disturbance is high. Generally, much of the world's forest land has been permanently converted to other uses such as food production and urban settlement, and therefore, are not likely to revert back to forest. Also, other areas of forest are needed for fiber production and other social and societal use, and increasing tree stocking and C density in this category can occur without negative effects on provision of other services. Currently, tropical forests are subjected to highest level of deforestation, and therefore, account for nearly all net emissions from forests. Large quantities of C are released when forests are cleared and burnt, and more GHGs are emitted from subsequent land uses after conversion from forest to the land uses such as agriculture. Industrial agriculture and commercial logging are the main drivers of deforestation and degradation, especially in tropical South America and Southeast Asia, the hotspots for forest-related CO_2 emissions. Emissions from land use change have been declining since 1990. However, this trend is misleading, because emission from other have been increasing at higher rates. Although several attempts have been made to estimate the forest potential mitigation, important C accounting considerations regarding forests is still lacking. This include C that is removed from forest in harvest operation and retained in wood products pools or discarded in landfills, which is not immediately returned to the atmosphere. Another C pool which is not fully accounted for is the substitution for using wood instead of other materials for construction which is not generally documented. These limits the ability of conducting lifecycle analysis to determine the energy consumption, emissions and sequestration throughout the full cycle of growing, harvesting, and processing wood compared to other materials. Compared to other mitigation strategies, forest-related activities, especially reducing emissions from tropical deforestation are among the most economically feasible and cost-effective options and the most viable strategy in the land sector. Reducing CO_2 emissions from forestry plays a relatively large role in reducing total CO_2 emissions in the short term and buy time to develop other mitigation and adaptation strategies. Forests are already removing significant quantities of CO_2 from the atmosphere naturally, which, coupled with other mitigation strategies remains essential for meeting long-term climate targets.

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Chapter 12
The Role of Bioenergy in Mitigating Climate Change

Abstract The combustion of fossil fuels drive the steady increase in greenhouse gases (GHG) and global temperatures observed in recent decades. The realization of adverse effects of increase in GHG emissions on the environment, the desire to limit atmospheric CO_2 concentration at 450 ppm or lower and limit global temperature increase to ≤ 2 °C, combined with increasing energy needs have made the quest for sustainable and environmentally benign sources of energy for industrial economies and consumer societies a high priority since 1980s. To limit atmospheric CO_2 concentration at 450 ppm, a total CO_2 emission reduction of 50–85% is required by 2050. As a result, there are a renewed interests in carbon-neutral or carbon-negative renewable energy sources. Among the renewable energy sources, biofuels are considered as an attractive fuel sources for replacing fossil fuels. Bioenergy is important for many sectors and mitigation perspectives as well as from the perspective of developmental goals such as energy security and rural development. It is argued that increasing the contribution of biofuels will reduce the GHG emission by reducing the carbon intensity of the transport sector and addressing energy security concerns. In addition to global climate change threat, interests in biofuels are enhanced by growing global energy demand and diminishing crude oil supply. However, there is concern about the existing interlink between biomass, bioenergy, land use, food supply, water use, and biodiversity. The first generation biofuels primarily produced from food crops feedstock are unsustainable due to the potential stress their production places on food, feed and fiber production. The second and third generation biofuels produced from abundant biomass and algae respectively are seen as the attractive solution to limitations of the first generation biofuels and also have higher potential for GHG emission mitigation. Yet, the practicalities of deployment of bioenergy at a large scale are mired in controversies over the potential resource conflicts that might occur, particularly over land, water and biodiversity. Additionally, a number of technical huddles must be overcome before their true potential can fully be realized and evaluated. This chapter summarizes the current knowledge of biofuels, the potential role in mitigating GHG emission, societal dilemma in large scale biofuel production, current assumptions on which global bioenergy resource estimates are predicted and future directions of biofuels research with the emphasis on assessments informed by empirical studies.

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Keywords Biomass · Biomass resources potential · Biofuels · Renewable energy · Carbon offsets · Biorefinery · Greenhouse gases

Contents

12.1 Introduction

All societies need energy to meet the basic human needs of cooking, space comfort, mobility, and communication. Energy is central to everything we do, as individuals, businesses, or governments—goods and services depend on access to energy. The quality of energy is important to the development process (Kaufmann 2004). For the sustainable development, delivery of energy services needs to be secure and have low environmental impacts. To be environmentally benign, energy services must have low environmental impacts, including greenhouse gases (GHGs) emission.

Much of the early development of mankind was fueled by the energy stored in plant biomass, mostly released by combustion and converted into increasingly sophisticated ways such as the use of steam engines. Industrial revolution gained momentum due to discovery and exploitation of fixed carbon molecules stored in the form of fossil fuels—primarily coal and petroleum. The fossil reserves of coal, oil and natural gas, which are the products of historic photosynthesis, were stored over millions of years, and they are the indispensable resources whose availability has been integral to the rapid technological progresses over the past few centuries. Currently they supply 81.6% of the global energy requirements (IEA 2016a). In addition to energy supply, fossil fuels are also important feedstock for industrial commodity products such as plastics, synthetic fabrics, rubber, lubricants, waxes, detergents, petrochemical coke, asphalt, solvent, fertilizers, pesticides, and pharmaceuticals (Bender 2000; Naik et al. 2010).

The availability of cheap fossil fuels from crude oil, coal, and natural gas in the twentieth century allowed the development of petroleum refinery system which also produces feedstock for chemical industry to meet the demand for growing population. However, in this century, these fossil resources are regarded as unsustainable, due to: (1) increasing demand for clean energy, and the associated economic instability which may occur as societies transition to environmentally compatible fuels, and (2) substantial environmental impacts associated with their use. The burning of fossil fuel is the big contributor to increasing atmospheric CO_2 concentration and associated global warming. Global energy policy is shaped by the rapid increase in demand for petroleum commodity as more nations become industrialized and economically affluent (e.g., China, India, and Brazil).

Meeting global energy demand in the future is one of the major topics of discussion due to the fact that the world population is growing, and is projected to reach 8.5 billion people by the year 2030 and 9.7 by 2050 (U.N. 2015). The majority of population growth is expected to occur in the developing world—Africa and Asia. Concurrent with the population growth in the developing world is the increase in standard of living in some countries with large population—notably China and India, and energy need for fuels, power generation, transportation, powering equipment, and other uses. In addition to its negative impact on global climate, the growing global consumption of fossil fuel resources is driving the paradigm shift to displace the fossil fuels with more sustainable, economically viable, and environmentally-friendly clean renewable energy sources to bring energy stability and security. Replacements for fossil-based fuels with cleaner renewable fuels is also of considerable interest to both global consumers and governments so as to maintain the safe atmospheric concentration of greenhouse gases (GHG) to limit global temperature increases to within the safe limits of ≤ 2 °C. As a result, policy makers are more willing to develop policies that promote potential solutions to these concerns. Therefore, the question is not if we should develop the alternative energy sources, or whether alternative energy is economically competitive with fossil energy sources, but how can we use alternative energy in a sustainable way, both economically, socially, and ecologically.

Human energy consumption can be grouped under heat, grid electricity and transportation fuels, and each of these is affected by different set of considerations which define the available options for improving sustainability and minimizing environmental impacts. Among the alternative renewable energy sources, biomass-derived energy appears to be the most attractive. While biomass can be directly burned to generate heat and electricity (Fig. 12.1), it is its contribution in transportation fuels where it has the opportunity to make a big impact through serving as feedstock to be converted to various liquid or gaseous fuels for practical applications. The current emerging strategy is to develop biorefinery and biomass transformation technologies to convert renewable biomass feedstock into clean energy fuels and other commodities which can substitute petrochemicals (Kamm and Kamm 2004; An et al. 2011; Volsky and Smithhart 2011). Biomass energy or bioenergy is the energy sources derived from plants, algal cells, and biological wastes, and residues associated with their processing such as agricultural residues, forestry and municipal wastes. Biomass is formed by plants and algal cells through photosynthesis; the natural energy transformation process that uses sunlight to concentrate atmospheric CO_2-C by over 1000-fold to chemical energy in carbohydrate (CH_2O)

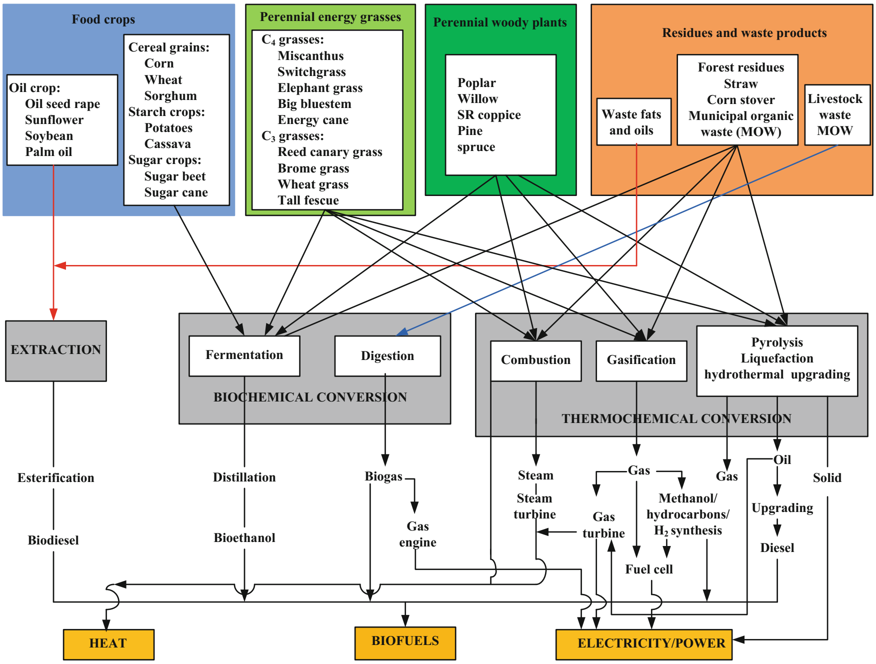

Fig. 12.1 Biomass energy feedstock and various conversion routes, adapted from Chum et al. (2011), Bessou et al. (2011)

(Karp and Shield 2008; Abdeshahian et al. 2010). This energy is then gradually released again through the metabolism of these energy-rich molecules.

When the biomass is used for energy, CO_2 is released which can be recycled to produce new biomass. Theoretically, no additional GHG is produced, since the emitted CO_2 is part of the existing C cycle. Therefore, if efficiently utilized, biomass can be regarded as renewable clean energy source due to its abundance. Biomass can be ‘carbon (C) neutral’ or even C negative depending on biomass production cycle and the process utilized to convert it to energy carriers. Bioenergy has significant GHG mitigation potential provided that the biomass feedstock resources are developed sustainably. In addition to being environmentally cleaner energy, biofuels can contribute to stabilization of farmers’ incomes and maintain ecological and social sustainability (Zhao et al. 2009), while also sequestering soil organic carbon (SOC) if suitable land and management practices are used for energy crop production.

Bioenergy is widely considered as the renewable energy sources which can fulfil the need of replacing fossil fuels for transportation and power generation without major economic investments in its production and distribution. As a result, bioenergy is being promoted through policy decisions at the national and regional level as one of the alternatives to fossil fuels. Bioenergy can provide energy independence and mitigate CO_2 emissions in short and medium term to allow transition to cleaner C free sources. Many studies on the future of energy systems also expect the bioenergy to play significant role in decreasing fossil fuels dependence as well as mitigating CO_2 emissions (Fisher et al. 2007; Dornburg et al. 2010; Chum et al. 2011). Large-scale production of renewable heat, electricity and transport fuels from biomass is important component in many climate change mitigation and resource supply scenarios (IEA 2011, 2016b; IPCC 2014). Liquid transport fuels account for approximately 30% of the CO_2 emissions in the industrialized countries, making them the major target in the drive to cut CO_2 emissions and increase sustainability in fuels supply.

In contrast to nuclear, Hydro power, wind and photovoltaic energy, biomass energy can be stored as solid, liquid, and gas energy carriers (DOE 2011). Bioenergy is the only alternative energy capable of replacing fossil fuels to support the mobility on a large scale (Wyman 2008) and also substitute production of byproducts produced from fossil fuels. Development of bio-based biorefinery has two strategic goals. The first goal of generating liquid fuels for displacement of petroleum fuels in favor of renewable and sustainable energy—(i.e., energy goal) is addressed by current efforts on ethanol, biodiesel and advanced biofuels. The second goal is to develop bio-based chemical products which could substitute for products produced from fossil fuels and offer higher return on investment, while meeting energy and economic goals simultaneously (Bozell and Petersen 2010).

Renewable energy sources contributed 79.3 exajoules (EJ, EJ = 10^{18} J) or 13.8% of the global primary energy production in year 2014 (Fig. 12.2a). Biomass-derived energy sources contributed 59.2 EJ yr^{-1} or 10.3%, mostly as biomass (55.7 EJ; Fig. 12.2b). This is 78% of the global renewable energy production, and it is the most widely used renewable energy source (Chum et al. 2011; Berndes et al. 2011; IEA 2016b). Biofuels contributed 2% of the liquid transport globally in 2011, while the rest was met by petroleum (IEA 2016b). Transportation fuels derived from biomass—biofuels is predominantly produced from conventional agricultural food crops feedstock. Transitioning to low-C energy economy while meeting increasing future energy demands require the rapid development of large global bioenergy sector capable of producing between 150 and 400 EJ yr^{-1} (van Vuuren et al. 2010a, b). Expansion of bioenergy production could increase energy security by reducing dependence on oil, natural gas and coal from limited regions (Ragauskas et al. 2006), while also creating employment to struggling rural economies and provide income opportunities to farmers in the developing economies and help alleviating poverty (Mathews 2007). However, the potential contribution from biomass to global energy supply is controversial. There are major concerns about the introduction of another land use sector which could accelerate deforestation, biodiversity loss and land degradation (Melillo et al. 2009) and competition for scarce water resources. Clearing C rich ecosystems for biomass plantations leads to substantial C loss from vegetation and soils into atmosphere which may take long time for the C debt to be offset, raising fear that the potential benefits offered by increase in biomass use will be outweighed by the environmental costs (Searchinger et al. 2008; Creutzig et al. 2012).

Biomass energy ranges from firewood used for cooking and heating to first generation biofuels—bioethanol and biodiesel produced from cereal grains, sugar

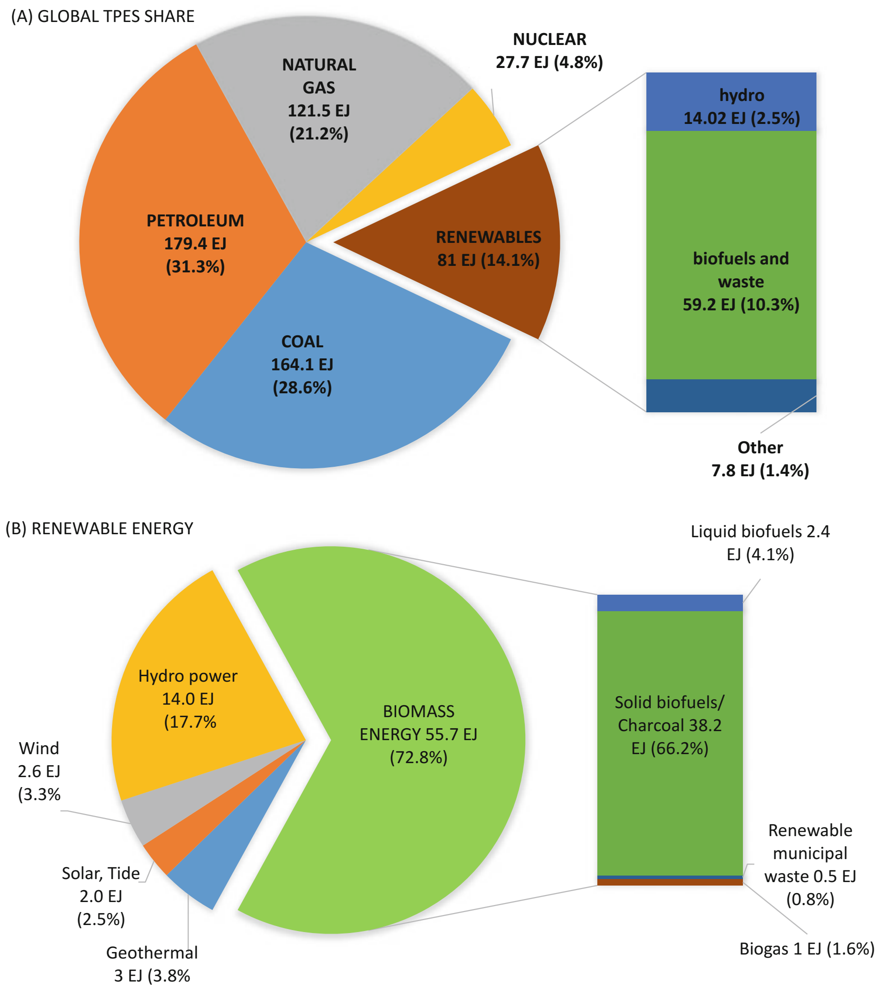

Fig. 12.2 Global shares of energy sources in total primary energy supply in 2011. Data from Chum et al. (2011), IEA (2016a, b, c)

cane (*Sacchurum* spp), sugar beet (*Beta vulgaris*), and oil crops; and the so called advanced fuels produced from plant biomass, as well as methane (CH_4) captured from landfills. Advanced bioenergy such as hydrogen (H_2) from engineered microorganisms, or electricity from photosynthetic cells which are being researched could also be considered as biomass energy (Field et al. 2008). Biomass is the oldest fuel used by mankind from the dawn of civilization. Prior to industrialization, biomass energy was the dominant source of energy globally, albeit in the form of fuel wood, agricultural residues, charcoal, and dung, for food and domestic purposes. Therefore, in comparison with current, the energy requirements were low with a growth rate almost parallel with that of global population (Hein 2005). Total primary energy consumption increased from the beginning of industrialization, coinciding with the discovery of coal in late 19th century, and continued to rise rapidly, particularly during the last six decades. This is mainly due to advances in productivity, mobility, and living standard. Global energy consumption increased 13-fold in the 20th century, and tripled since 1960, which is faster than the increase in population (Hein 2005). Global biomass consumption also increased from 1000 Tg yr^{-1} in 1850 to 2460 Tg yr^{-1} in the year 2000, responding to population growth in the developing world (Fernandes et al. 2007). Domestic use of biomass energy has always been important globally, and it continues to fulfil its traditional role as the main energy source in many parts of the developing world today. However, industrial uses, particularly in North America and Latin America have been expanding over the past century (Fernandes et al. 2007). It is frequently used as a source of industrial heat, especially in the forestry and paper industries (Farla et al. 1997). Renewed interest in bioenergy will likely maintain the increase in global biomass consumption for a foreseeable future.

12.2 Definitions

In this chapter, biomass energy is an all-embracing term that covers the production of heat, power, transport fuels, and other products from organic materials of recent origin (as opposed to fossil materials of geologic timescale). The term plant biomass typically refers to lignocellulose material as this makes up the majority of plant mass. Biorefinery is defined as the process of co-production of bio-based power, heat, and fuel energy carriers such as bioethanol, biomethanol, biodiesel, etc., with a spectrum of bio-based products—food, feed, chemicals, and other industrial materials from biomass. Bioenergy is confined to renewable energy from biological materials. However, terms bioenergy and biofuels are used interchangeably and defined as any fuel that is made from organic matter or biomass. Bioenergy is sometimes used with reference to renewable heat and power and sometimes it also include renewable transport fuels. In this chapter the former definition is adapted, and takes it to mean production of renewable energy from biological materials, and we reserve the use of the term biofuels for renewable liquid transport fuels. Bioenergy can be broadly classified as primary and secondary fuels. Primary fuels are natural unprocessed biomass used primarily for heat and power generation, such as fuel-wood, wood chips, pellets, etc. The secondary fuel is modified primary fuels which have been processed and produced as liquid (e.g., biofuels—ethanol, biodiesel, bio-oil), or gases (e.g., biogas, synthesis gas, hydrogen).

Biofuels are subdivided into bioethanol made from fermentation of carbohydrates which is a substitute for gasoline (petrol), and biodiesel made from vegetable oil is a substitute for diesel. Biofuel production from food commodities—carbohydrates/starches and oils—stored in forms that are easily accessible is referred to as first generation biofuel. This is because the fermentation of sugars and starches and trans-esterification of lipids and oils for biofuel production involves well-developed conversion technologies, the only change being that the product is used for transport rather than for human consumption. In contrast, second generation biofuel involves much more complex processes to break the recalcitrance of polysaccharides and lignin of the cell wall. Although cellulose materials represent an abundant potential source of sugars, the additional pretreatments and hydrolysis steps required to make stored carbohydrates accessible for energy processing are currently inefficient, energy-intensive and expensive, which present a major challenge to advance the second generation biofuel. Considerable optimization of the enzymatic and physicochemical processes is needed to improve the efficiency of the conversion chain. Similarly, the same is true for production of liquid fuels from gasification and pyrolysis of plant biomass.

12.3 General Background on Biofuels

As of 2014, global primary energy demand was 573.6 EJ yr^{-1} compared to 256 EJ yr^{-1} in 1973 (IEA 2016a). World energy demand is expected to increase to 765 EJ yr^{-1} by 2040, driven primarily by India, China, Africa, the Middle East and Southeast Asia (IEA 2016a, c). More than two thirds of the growth will come from the developing countries where economic and population growth are the highest (EU 2006). Current global energy supply is dominated by fossil fuels, contributing 81.1% of total primary energy in 2014, with smaller contribution from nuclear (4.8%) and hydro power (2.5%) (Fig. 12.2; IEA 2016a). Energy is also a large contributor of CO_2 emissions, emitting 15.5 Pg yr^{-1} CO_2 in 1973, which increased to 32.4 Pg yr^{-1} CO_2 in 2014 (IEA 2016a). Fossil fuels will continue to dominate global energy supply, meeting more than 80% of the projected increase in the primary energy demand for a foreseeable future.

Transport is major energy consumer, accounting for 27.9% of final energy consumption worldwide, and the two thirds of projected increase in energy demand will come from transportation sector (IEA 2016b). It is one of largest GHG emitter also, accounting for about 13.5% of global emission (Baumert et al. 2005). Fossil fuel burning emitted an average of 8.3 ± 0.7 Pg C yr^{-1} between 2002 and 2011 and cumulative of 375 ± 30 Pg C since the beginning of industrialization (Ciais et al. 2013). Current global oil reserves exceed the demand, but peak production is projected within the next two decades. Some experts argue that the world is already at peak production. Although the exact peak period is still debatable, it is generally accepted now that it will happen within the near future. In a post-peak scenario, the gap between supply capacity and demand could reach as high as 20% within 5 years based on current increase in both population and energy demand. Therefore, energy transition is unavoidable. The increased demand for the refined products can only be met with the additional capacity (IEA 2016b). To alleviate the uncertain future of energy supply, the global energy sector is investing on ambitious program of accelerating the development of advanced energy technologies in order to address global challenges of clean energy, climate change, and energy security, and maintain sustainable development with an overall goal of achieving 50% reduction of CO_2 emissions by 2050 over 2005 levels (IEA 2011).

Renewable energy is any energy that is replenished by natural processes at a rate that equals or exceeds its rate of use. It is obtained from continuing or repetitive flows of energy occurring in natural environment. Renewable energy sources play an important role in providing energy services in a sustainable manner while also mitigating climate change by replacing fossil fuel energy sources. It includes resources such as biomass, solar energy, geothermal energy, hydropower, tides, waves, and ocean thermal energy, and wind energy (Moomaw et al. 2011). Flow of resources such as wind and solar energies are non-limited resources, despite intermittence in their supply. In contrast, biomass resources are limited resources, and their availability depends on other natural resources such as land, water, ecosystems, regeneration rates, and anthropic production and consumption rates. The renewal of biomass depends on its management, which should ensure that primary resources are not overexploited or even depleted.

Increasing the share of the world energy that comes from renewable resources is critical in stabilizing global climate (IPCC 2012). Currently renewable energy is the fourth largest source of global total primary energy source after petroleum, natural gas, and coal, supplying 14.1% of total primary energy for the year 2014 (Fig. 12.3, IEA 2016a). Primary energy is the energy found in nature that has not been subjected

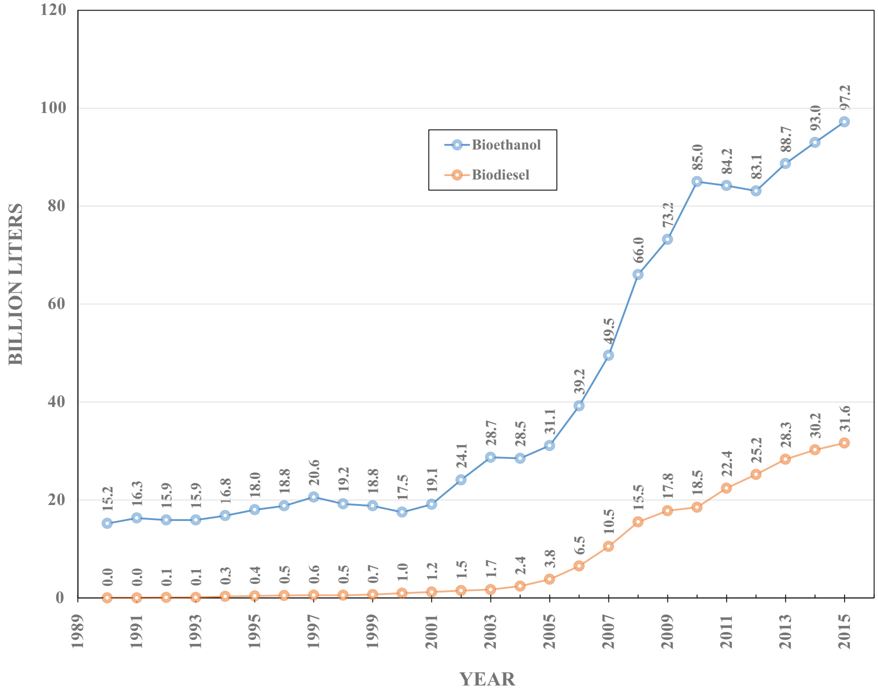

Fig. 12.3 Global biofuel production 1990–2012. *Data sources* IEA (2011, 2016b), BP (2015)

to any conversion or transformation processes. It is therefore, the energy contained in a raw fuels as well as other forms of energy received as an input to a system (FAO 2010). The share of renewables in primary energy use in the new policies scenarios is projected to rise and reach 18% by the year 2035 (IEA 2016b). Among the renewable energy sources, only biomass can provide liquid fuel and generate electricity in a form and scale compatible with the existing transportation and power generation infrastructure (DOE 2006). Analyses of global energy system transformation required in order to mitigate a dangerous climate change conclude that biomass energy will play an important role in the global energy mix of the next decades (van Vuuren et al. 2010a; IPCC 2012, 2014). Biofuels provide a way towards shifting to low-C non-petroleum fuels, generally with minimum changes to vehicle stocks and distribution infrastructure (IEA 2011). It is envisioned that significant reduction in CO_2 emissions could be achieved by improving vehicle efficiency, and increasing biofuels share of transport fuels from current 2 to 27% in 2050 (IEA 2011). Unlike wind and solar, biomass can be converted directly into liquid or gaseous fuels through various conversion routes and become usable as is current practice with petroleum and natural gas. It can also be stored and generate electricity on demand as is current practice with coal. It also provides raw material for renewable alternatives to fossil based products.

Energy crops are crops which are produced with express purpose of using their biomass for energy. High contents of lignin and cellulose in their biomass are the desirable characteristics for the energy plants, especially when the plant biomass is used as solid fuels for electric generation or heat, because they have a high heating value due to high content of C in lignin ($\sim$ 64%), and the ability to stand upright at a low water contents. Therefore, their biomass can dry on stem allowing late harvest for improved biomass quality. The biomass of perennial grasses has higher lignin and cellulose contents than that of annual crops. Because biomass such as trees and plants can be cultivated and harvested on regular basis, and be replenished, biomass energy is considered as a renewable energy source (Cook and Beyea 2000; Dalgaard et al. 2006; Berndes et al. 2003; Schuck 2006; DOE 2005; Nicholls et al. 2008). When used in a sustainable way, biomass represents a renewable energy which can be widely available due to its abundance ($\sim$ 100 and 50 billion tons of land and aquatic biomass, respectively produced on the biosphere), high energy content, biodegradable, and production of recyclable CO_2 (Srirangan et al. 2012). Biomass is usually considered a source of sustainable, cleaner energy for transport fuels and power generation.

There are many environmental, economic, and ecological benefits which can be gained from judicious production and use of energy generated from biomass (Table 12.1). Moreover, the recalcitrance of lignocellulose biomass is the main technological challenge which is currently making economic feasibility of biomass-derived biofuel too expensive to compete with existing fossil fuel technologies. The substitution of fossil fuels and/or raw materials based on fossil fuels by the biomass is one of its important contributions for reducing anthropogenic CO_2 emissions. Application of biotechnology and bioengineering both to bioengineered energy crops and microbial organisms used for the bioreactors is one of the important tools which can improve the conversion and increase the potential for biomass to significantly contribute to biofuel production.

Table 12.1 Potential benefits and limitations of biomass energy sources

Potential benefits	Potential limitations
Environmental gains • Reduced dependence on fossil fuels which has significant impacts on environment • Decreased greenhouse emissions • Reduction in smog and other harmful chemical emissions • Use of biological waste materials reduces need for landfill	Environmental threats • Depletion of local water supplies • Potential use of protected land for biomass supply • High demand for fertilizers, pesticides, herbicides may lead to air and soil pollution • Possibility of increasing greenhouse gas emissions associated with natural land clearing, land use change and increased fertilizers use • Potential effects on ecosystems • Reduced biodiversity due to industrial cultivation of favored energy crops • Increased particulate C emissions as a result of increased biomass burning
Economic benefits • Relatively cheaper resources • Locally available in many places which provides constancy and reliability • More widely distributed, which provides access to energy, increased energy independence and security • Provides energy price stability • Increased employment opportunities to rural communities • Provides biomass and bioenergy technology export opportunities • Makes use of underutilized biomass and land resources • Biomass resources are renewable	Technological limitations • Limitations associated with collection, transport and storage of feedstock • Pre-treatment of biomass may cause C debt in terms of energy and chemicals required • Enzymes production may also limit the conversion process and limit the production of biofuels from environmentally friendly, economically sustainable and socially acceptable biomass • High cost of the technology for manufacturing and maintenance of biofuel processing facilities
Ecological benefits • Replacement of intensive agriculture with perennial biomass crop will benefit the biodiversity and provide ecological benefits • Reduction of climate change effects on biodiversity in the long-run due to reduced GHG emissions • Restoration of marginal land where these lands are used for biomass production	Ecological challenges • Large-scale land acquisition • Land use change of natural habitat and other ecologically valuable land acquired for biomass production • Biodiversity and water preservation challenge

12.4 Role of Biomass Crops

Various alternatives for fossil fuels for heat and power generation exist, e.g., wind, hyro, solar, as well as plant biomass—are expected to play role. However, there are only few alternatives to replace transportation fuels—e.g., electric and hydrogen. As the number of vehicles on roads continues to increase, especially in the developing countries due to improving standard of living, it is becoming clearer that unless the emissions from the transport sector can be curbed, they will counter any reductions achieved in other economic sectors. In addition, combination of the desire of some countries to reduce their reliance on fossil fuel supply from only few major producers, and also to boost rural agricultural economies has resulted in a swift and strong push to increase the production of liquid transport fuels from crops, and many food crops have been exploited and continues to be exploited for this purpose. Simultaneously, the need for large range of chemicals and industrial products that currently rely on the refining of crude oil is becoming apparent to the chemical processing industries. Combination of the environmental, political, and economic drivers have led to emergence of three new large markets for biomass resources: (i) reliable renewable energy supply, (ii) biofuels for transport, and (iii) biorenewable chemical supply. Moreover, securing sufficient food for current and future populations remains a main challenge, particularly in the face of climate change and the associated uncertainties. To balance all these demands on plants and the associated land resources necessitates another green revolution.

Although biomass production is a solution to these challenges, the feasibility and social, economic, and environmental impacts of a large scale biomass production for energy feedstock has been a topic of contentious discussion and investigation by many researchers (Fargione et al. 2008a; Searchinger et al. 2008; Hill et al. 2009; Kim et al. 2009; Levasseur et al. 2010; Smeets and Faaij 2010; Solomon 2010; Taheripour et al. 2011; Dohleman et al. 2010; Hertel et al. 2010; Blanco-Canqui 2010; Bonin and Lal 2012). It is also argued that agriculture is a major user of resource, including energy from fossil fuel, and also a major contributor to GHG emissions. It is also pointed out that producing energy from biomass could have the unintended effect of increasing GHG emissions if the inputs and GHG emissions associated with any new cultivation for displaced food production exceed the carbon offsets by the energy produced (Searchinger et al. 2008). Others have raised major ethical and environmental points that biofuel production using food crops as feedstock raises ethical question of choice between food-versus-fuel debates (Tilman et al. 2009). In addition, use of crop residues depletes soil nutrients, impacts soil properties and sustainability (Blanco-Canqui 2010; Bonin and Lal 2012), while energy crops compete with food and feed production for fertile arable croplands, and causes direct or indirect land use change (Fargione et al. 2008b). Some authors have argued that energy generated from plant biomass is close to ‘C-neutral’ because the CO_2 released in the process is the same as that captured by plant photosynthesis, while preserving C stored in fossil reserves (Sims et al. 2006). Also, when natural land is converted into arable energy crops, increased pollution from fertilizers and pesticides, GHG, soil erosion, and decreased biodiversity can result (Pimentel 2003). The emerging general consensus from the research is that the resources are limited, future expansion of biofuels must be sustainable, and must have minimum environmental, and diversity impact. Nevertheless, the research emphasis should be on improving the entire chain from crop characteristics through breeding, biotechnology and bioengineering, production chain through best agronomic practices, and finally fuel processing efficiency. Biofuels debate took a turn following a publication by Searchinger et al. (2008) which pointed out that the increase in the use of corn grains for bioethanol would result in new planting of corn around the world to make up for the decrease in food and that the GHG emissions resulting from this new land conversion would result in C debt which cannot be offset by savings gained from fossil fuel replacement by biofuel. Although the assumptions made in the argument have been challenged by other researchers, the momentum shift caused by their argument has been slow to recover, and the current general consensus is that of ‘caution’.

It is recognized that efficient lignocellulosic biomass (i.e., a structural material that account for much of the plant mass) processing system which can hydrolyze and ferment cellulose and hemicellulose—the polysaccharide of the plant cell wall of the plant biomass for commercial production of lignocellosic biofuel will have significantly higher fossil fuel emission reduction potential than food crops. In addition to recycling atmospheric CO_2, plant biomass fuels can achieve a reduction in GHGs by sequestering C into soil ecosystem (Ceotto 2008; Benbi and Brar 2009; Anderson-Teixeira et al. 2009). Sequestration of atmospheric CO_2 into the soil is beneficial to many ecosystem functions and services including increased productivity, improved water and nutrients retention, and increased biodiversity.

Dedicated energy crops are of particular interest for the production of biofuel using lignocelluloses. One benefit of lignocellulosic biofuel is that it can be produced from abundant and diverse feedstock including grasses, wood, and non-edible parts of crop plants. Perennial plants are associated with good environmental performance and improved ecosystem health than annual crops currently in use for generation of biofuels. Because there is no annual tillage involved, their belowground biomass accumulates and protect soils against wind and water erosion while also improving soil quality and storing SOC in deeper soil layers (Luo et al. 2010). Lack of annual tillage also minimizes fuel usage in production chain and improves overall energy balance of fuel production. Low input perennials need to be planted only once, and require minimum inputs.

Establishing biofuel plantation on degraded and marginal lands can yield important co-benefits of C sequestration and restoration of degraded/marginal land in addition to biofuel production. The lifecycle analysis (LCA) of biofuels needs to also take account the changes in SOC associated with biofuels plantations in all bioenergy production scenarios. LCA is a computational tool used to evaluate the sustainability of a future biofuel industry along its partial or whole lifecycle, covering the environmental impacts generated from cradle to grave. Biofuels can contribute to reducing the dependency on fossil fuels and lower GHG emissions from transport if the saving in CO_2 emission through the use of biofuels is not counterbalanced by an increase in GHG emissions during biomass crop production and energy required during transformation of the biomass to transport fuel. Biomass is also the only available source of renewable C for products currently made from fossil sources. Biomass therefore provides diverse bioenergy chains and various bio-products. The diversity of raw materials and transformation processes offer a wide range of possibilities that can be adopted to different geographical locations, and energy needs.

12.5 History of Biofuels

Low efficiency (10–20%) traditional biomass such as wood, straw, charcoal and dung are used for domestic purposes such as cooking, lighting, and space heating, generally in developing countries. Until mid-1980s' traditional biomass accounted for a large proportion of household energy needs (Yevich and Logan 2003), albeit with severe air pollutants and health consequences (Streets et al. 2003). High efficiency (58%) modern bioenergy utilizes solid, liquid and gases as energy carriers to generate heat, electricity, combined heat and power (CHP) for various sectors and transport fuels (Chum et al. 2011). It includes liquid biofuels—ethanol and biodiesel that are used for road transportation and some industrial uses. Biomass-derived gases (primarily methane and biogas) from anaerobic digestion of agricultural residues and waste treatment streams are generally used to generate electricity, heat or CHP for various sectors. There is rapid expansion of modern biomass energy use worldwide, especially biofuel for transport in response to policies specifically aiming at improving energy security and mitigating climate change.

Use of biofuels in the transportation is not a new discovery. Liquid biofuels for transport have been used since the early days of the automobile industry. The use of alcohol as a fuel is as old as the discovery of the internal combustion engine. The earliest internal combustion engines developed by earlier pioneers such as Nikolaus Otto and other 19th century inventors were designed to run on alcohol (Bernton et al. 1982). By 1880s, alcohol powered engines were popular enough to replace steam engines in light machinery, pumps, and locomotives, including automobiles in Europe and United States (Bernton et al. 1982). By the turn of the century, the alcohol powered engines were advertised to be safer than the steam engines because they did not produce fire triggering sparks. Many European governments with few oil reserves encouraged the development of fuels that could readily be distilled from domestic farm products. For example, German government worked closely with its distilling industry to pass legislation providing financial incentives to produce alcohol and create markets for its industrial use.

Similarly, the idea of using vegetable oil for fuel is as old as the diesel engine. Rudolf Diesel (1858–1913), the inventor of the compression engine that bears his name, experimented with fuels ranging from powered coal to peanut oil (Radich 2004). Many vegetable oils were investigated for fuel during the historic times—including palm oil (*Arecaceae* spp), soybean oil (*Glycine max*), cottonseed oil (*Gossypium hirsutum*), castor oil (*Ricinus communis*), etc. The early publications indicated satisfactory performance of vegetable oils as fuel for diesel engines (Knothe and Krahl 2005). During his education at the school predecessor to Technical University of Munich in 1878, Rudolf Diesel was introduced to the work of Carnot, who theorized that an engine could achieve much higher efficiency than the steam engines of that day if the gas is compressed, heated, allowed to expand and then cooled, and then the cycle begins again. Carnot envisioned the use of mechanical energy to compress the gas and thermal energy to heat it, and in turn, the expansion of gas yields mechanical energy, while its cooling will yield thermal energy with the net result of converting thermal energy to mechanical energy (Deusche Museum website). Rudolf Diesel sought to apply Carnot's theory to the internal combustion engine, the predecessor of the modern internal combustion engine, which was invented by Nikolaus Otto in 1876. Diesel sought to build an engine with the highest compression ratio as opposed to Otto's low compression ratio internal combustion engine. In his design, he introduced fuel only when the combustion was desired and allowed fuel to ignite on its own in hot compressed air. He demonstrated the working engine in 1897, and used peanut oil in the first demonstration of his compression engine on peanut oil for the 1900 World Fair exhibition in Paris (Knothe 2001; IEA 2011). Use of vegetable oils was widely promoted to provide the European tropical colonies, especially those in Africa with the degree of energy self-sufficiency (Knothe 2001). Vegetable oils were also used as emergency fuels during World War II. During 1940s, Belgium, France, Italy, the United Kingdom, and Germany each investigated the use of vegetable oil fuels, and during the WW II, Brazil, Argentina, Japan, and China used vegetable oil as fuel (Knothe 2001). Vegetable oils were used in diesel engines until 1920s. The introduction of gasoline powered automobiles obliged the oil companies to refine much crude oil to supply gasoline, which left so much surplus of the distillate which was less expensive than the vegetable oils. Therefore, the alterations were made in the diesel engines enabling it to use residual petroleum which is now known as diesel fuel.

Demand for fossil resources has always been a concern with the regard to petroleum fuels. Also, farmers have always sought new markets for their products. Consequently, research has been continued on the use of vegetable oil and ethanol as fuel. Durability tests of the altered diesel engines showed that these engines will fail prematurely when operating on vegetable oil. However, if vegetable oil has been transesterified with alcohol, engines exhibited no such problems. In some measures, they performed better than engines using petroleum diesel. These tests became the basis of the current thrust of biodiesel.

Henry Ford was also convinced that renewable resources were the key to the success of his automobiles such that he designed Ford Model T of 1908–1926 capable of running on ethanol. His vision was to build a vehicle affordable to the working family and powered by a fuel that would boost the rural farm economy. He also built ethanol plant in Midwest and established partnership with Standard Oil Company to sell it in their distribution stations. Bioethanol-gasoline blends have long history as alternative transportation fuels also. At the beginning of World War II, both Germany and Allied Forces utilized biomass fuels in the machines. Wartime Germany experienced a severe shortage of oil. The vehicles were powered with blends including Reichskerafspit, which was a blend of gasoline and alcohol fermented from potatoes (*Solanum tuberosum*). In Britain, grain alcohol was blended with petrol by Distillers Company Ltd under the name of Discol and marketed through Esso affiliate—Cleveland. Until the 1940s', biofuels were considered as viable transport fuels (IEA 2011). However, after WWII, biofuels remained under obscurity, and the availability of cheap petroleum increasingly replaced biofuel in transportation and industrial products (Morris and Ahmed

1992). Therefore, the biofuel technologies were not advanced because of relatively higher production costs compared to fossil fuels. The stable petroleum based industry made biofuels a forgotten product until the oil crises of 1970s'.

Interests in biofuels were reignited by legislative, political, and economic concerns in 1970s. For example, in the USA, the passage of Clean Air Act in 1970 allowed the Environmental Protection Agency (USEPA) to regulate emission standards for pollutants such as sulfur dioxide (SO_2), carbon monoxide (CO), ground level ozone (O_3), nitrogen oxides (NO_x), and particulate matter. This provided the incentive for research to develop cleaner burning fuels. In addition, in 1973–1974, the Organization of Petroleum Exporting Countries (OPEC) that controls the majority of the global oil production reduced the supply crude oil—(oil embargo) and increased prices of crude oil by 135%. This had a major impact on the world economy, due to the importance of petroleum products to the society. The second oil crisis came in 1979 caused by Iran Revolution. These made many countries to consider alternative fuels to substitute fossil fuel. In 1970s, Brazil started commercial production of ethanol from sugar cane (*Saccharum* spp), and the USA started commercial production of ethanol from corn. Since 1980s, there has been an increased global interest in the use of bioethanol and biodiesel in the transportation sector.

Major challenges to the modern world and their way of life have become the focus of public interest in biofuels: (i) worries about the energy security, (ii) interest in economic development in both developed and developing world, (iii) creation of sustaining jobs in rural agricultural communities, and (iv) the need to control the increasing GHG emissions and mitigate the climate change. Fuels made from locally grown renewable sources are being advocated as solution to these four challenges. In addition, bioethanol and biodiesel are been promoted for the substitution of the expensive imported crude oil, to address the health concerns associated with air pollution, leaded (Pb) fuels, octane and cetane boosters, unsustainable farming subsidies, among other reasons. In the most parts of the world, the fastest growth in biofuel production has taken place since the year 2005 (Fig. 12.3) supported by ambitious government policies. The two commonly used measures to boost the biofuel production and use are tax incentives and blending mandate, which guarantees the markets and become incentive for the private sector investments.

Worldwide, liquid biofuels comprise a small (4.1% in 2014) (IEA 2016b), but growing total primary energy supply (Chum et al. 2011). Under new policies scenario, biofuels could account for 12–15% of the energy consumption in the transportation sector by the year 2035 (IEA 2016b). It is generally accepted that peak oil supply will occur sometime in the future, and transition from petroleum products for energy is unavoidable. Diversifying the energy mix now with a growing contribution from cleaner sources is important for both the environment and future economic stability (Bessou et al. 2011). It is also an important step towards transitioning to clean C-free energy sources. Biofuels are one of the renewable alternative which can potentially be cleaner energy and capable of mitigating CO_2 emissions provided that the savings in CO_2 emissions through

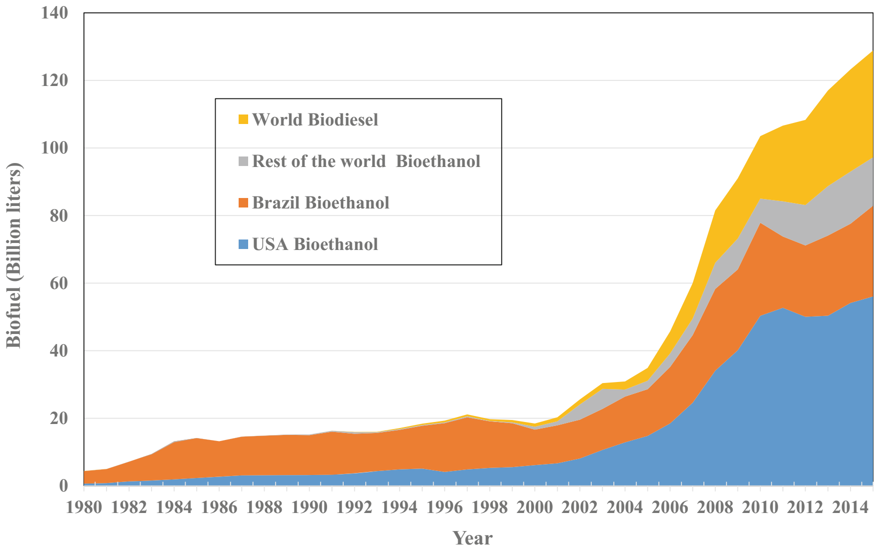

Fig. 12.4 Global biofuel production from 1980 to 2012. *Data source* IEA (2011, 2016b), BP (2015)

biofuels is not offset by an increase in emissions of other GHGs during the biomass production chain, processing, and transformation of biomass to usable energy.

Currently, bioenergy industry is dominated by biofuels made from first generation feedstock options which vary by country: the US uses corn grain; Brazil relies on sugarcane, while European Union is the main producer of biodiesel from rape seed oil, and these accounts for >80% of biofuels currently in the market (Fig. 12.4). Most of US biofuel is ethanol produced from corn starch, and as the US ethanol industry continues to grow over the years, so too is the usage of annual corn grain crop. For example, in 2000 ethanol production was using about 6% of corn grain supply, and by the year 2015 reached nearly 40% of US corn grain, based on current corn grain production. Although corn ethanol is capped at 56.8 billion liters (L) from 2015 onwards, under existing corn production, it means that ethanol production will continue to use about 40% of US corn grain production for many years to come, depending on yield increase and production area expansion. Some of the consequences of increased usage of corn grains for biofuel production are: (a) competition of arable cropland between corn and other field crops, which could result in more intense agricultural activity on US cropland to meet growing demand for food, feed, and fuel resources, (b) corn is more input intensive than other major field crops, which could result into environment and water pollution from fertilizers, pesticides and herbicides use, (c) impacts on water resources availability and quality as a result of demand for irrigation water and high usage of fertilizers, (d) impact on soil fertility and sustainability as a result of intensive agriculture, and (e) impact on soil conservation practices.

In summary, production of biofuels from existing food crops such as corn grain, oil seeds, or even crop residues such as corn stover have a number of disadvantages. Most of annual crops require large inputs of energy in cultivation and planting each year. Also, much of the increase in yields which have been achieved over the past 50 years have resulted from breeding for improved partitioning of total biomass into grain and increased grain yield as a direct response to added fertilizer N and P. Since the entire aboveground biomass is used for energy, partitioning of biomass to grain is of no relevance for dedicated energy crop. The key consideration in fuel crop is their energy balance (i.e., energy in: energy out). Additionally, N fertilizers require large inputs of energy during their production. For example, 35.34 gigajoules (GJ, GJ = 10^9 J) of natural gas are needed to produce 0.9 megagram (Mg) of anhydrous ammonia (Huang 2007), and more energy is needed for its transportation and frequent N application. Moreover, a high N content in the harvested biomass is undesirable because of its implications for NO_x pollution during energy consumption.

Other harmful effects of food crop biofuels include: (i) the C debt created by land clearing elsewhere to replace the displaced food production (Kline and Dale 2008; Searchinger et al. 2008; Fargione et al. 2008b), (ii) intensive farming of the existing arable lands and extraction of biomass has the environmental consequences of increased soil erosion, greater NO_3^- leaching, loss of P and other plant nutrients, impact to ground and surface waters, air quality and biodiversity (Robertson et al. 2008).

Although there are high interests in cellulosic feedstock for biofuels, the current investment in the infrastructure for grain biofuel processing, especially in USA suggests that production of bioethanol from grain will continue to consume a substantial portion of corn production for a foreseeable future. Therefore, in addition to current research focusing on lignocellulosic biomass production and processing techniques, it is important to consider some ways to minimize the environmental impacts of intensive grain production. Some land management techniques such as no-till (NT) farming, and cover crops can minimize soil erosion and build SOC. In addition, advanced fertilizer technologies can improve crop N use efficiency and reduce N leaching and also minimize N_2O emissions. Riparian buffers and unmanaged habitats can protect natural water ways from runoff and leaching and also support pollinators and wildlife while also maintaining biodiversity.

12.6 Bioenergy Resources Potential

Production of bioenergy crops interacts with food, feed, fodder, and fiber as well as forest products in a complex ways. In one way, bioenergy demand constitutes a benefit to conventional plant production in conventional agriculture and forestry by offering new markets for biomass flows that were not existing. Some of the biomass utilized in energy were considered waste products or of low value. Bioenergy can also provide the opportunity of cultivating new types of crops and integrating it with food and forestry production, which can improve overall resource management. In contrast, biomass production for energy can intensify competition for land, water, labor, and other resources and production factors. It can also result into overexploitation and degradation of production resources. For example, over-extraction of biomass from the land can lead to soil erosion and degradation, water diversion to energy plantations which can impact downstream, and regional ecological functions and economic services. Also, converting food products such as carbohydrates and/or plant oils into ethanol and biodiesel have limited emission mitigation (Fargione et al. 2008b). Bioenergy production also compete directly with food production for most fertile lands (Searchinger et al. 2008; Melillo et al. 2009; Lapola et al. 2010). The biomass resource potential depends on the priority given to bioenergy products versus other products obtained from the land, notably food, feed, fodder, fiber, and conventional forest products such as saw wood, and paper, and how much biomass can be mobilized from agriculture and forestry without impacting land sustainability and other ecosystem services. This will depend on natural conditions—climate, soils, topography, agronomic and forest management practices and the prioritization of nature, soil, water, and biodiversity conservation by the individual societies, and how the production systems are shaped to reflect these priorities.

Even though the environmental sustainability of large-scale bioenergy production raises serious questions, the technology is still regarded as key bridging technology during the transformation towards a low-C economy due to its potential to deliver C-neutral and even C-negative emissions at comparatively low costs required for substantial emission reductions (WBGU 2009). In this context, sustainable energy potential estimates on the basis of land use restrictions to avoid additional GHG emissions, and biodiversity loss and other environmental and agricultural impacts have been made. Assessment of resources potential quantifies the availability of residue flows in the food and forest sectors by taking into consideration the environmental and socioeconomic factors which adjusts the assessed potentials to the lower values. Global productive land area is estimated at 82.37×10^6 to 130.4×10^6 km^2 (Table 12.2, Beringer et al. 2011; Haberl et al. 2010), which include cropland, grazing land, and forest land. The global total annual aboveground net primary production [(NPP), i.e., the net amount of C assimilated by the vegetation on Earth's terrestrial surface] is estimated to be 35×10^3 Tg of C, assuming an average C content of 50%. Assuming heating value of 18 GJ Mg^{-1}, this produces 1260 EJ yr^{-1} as a theoretical biomass resource potential (Haberl et al. 2007, 2010). About 25% of the Earth's land is devoid of human use, and it generates about 11% of NPP (Table 12.2).

The aboveground NPP of cropland and grazing land amounts to 574 EJ yr^{-1}, of which, human currently harvest 217 EJ yr^{-1} for food, feed, fiber, and bioenergy, including 28 EJ yr^{-1} of unused cropland residues (Haberl et al. 2007; Krausmann et al. 2008). Global industrial round-wood harvested corresponds to 15–20 EJ yr^{-1}, and global harvested major crops—cereals, oil crops, sugar crops, root, tubers, and pulses—correspond to 60 EJ yr^{-1} (FAOSTAT 2016). Up to 70 EJ yr^{-1} is burned in human-induced fires (Lauk and Erb 2009). The cropland area is projected to expand by 9%, and average yields on cropland is projected to increase by 54% in 2050 compared to 2000 cropland area and yields, respectively (FAO 2012). Based on these estimates, the biomass productivity and extraction from agriculture and forest will have to increase tremendously in order to provide feedstock for bioenergy sector large enough to significantly contribute to energy supply.

Societies around the globe are already appropriating a substantial share of the world's aboveground terrestrial NPP. For example, Haberl et al. (2007) estimated that human appropriation of terrestrial NPP across all human uses of biomass in the year 2000 was about 29% of the modelled global aboveground NPP. Biomass harvested by human (including residues used for grazing) accounted for 20%, and energy content of 219 EJ yr^{-1} (Krausmann et al. 2008). In addition to biophysical factors discussed, socioeconomic conditions play significant role in defining how, and how much biomass can be produced without causing severe socioeconomic impacts considered unacceptable. The socioeconomic conditions vary around the world, and also change as the societies develop. It also depends on how societies prioritize bioenergy relative to other socioeconomic objectives. The pattern of energy use in the world is changing with successive industrialization of the economies of the developing world. This has driven an increase in the demand for energy and the fossil fuel, at the rate of 1.9% yr^{-1} from 1973 to 2014 (IEA 2016a, b). Scenarios for increasing bioenergy deployment are contingent on the anticipated food and energy demand, environmental protection, and expectations for technological advances—including economical biorefinery and biomass-to-biofuel conversion technologies (Slade et al. 2014).

Biomass production potential is generally estimated in hierarchical order—theoretical > geographical or technical > economic > realistic or implementable. However, the terminologies are not always used consistently in the literature. Assessment of biomass production technical potential takes into consideration the limitations of biomass production practices assumed to be employed and the concurrent demand for food, feed, fodder, fiber, forest products, and area requirements for human infrastructure. In some cases, restrictions posed by nature conservation,

Table 12.2 Global land area and its net primary productivity (NPP)

Land use category	Area ($km^2 \times 10^6$)	NPP (EJ yr^{-1})	Aboveground productivity (MJ m^2 yr^{-1})
Urban areas	1.4	6	4.6
Cropland	15.2	196	8.1
Grazing land	46.8	379	12.8
Forest land (human used)	35.0	520	14.9
Unused productive land	15.8	137	8.7
Unproductive land	16.2	2	0.1
Global total (excluding Greenland and Antarctica)	120.4	1239	9.5

soil, water, and biodiversity are also taken into consideration. When these restrictions are taken into consideration, the technical potential becomes sustainable potential. In contrast, theoretical potential assesses the potential biomass supply based on biophysical limitations only. Theoretical potential is generally higher than the technical potential. The technical and sustainable assumptions behind the estimated potentials reported in the published literature are primarily driven by the choice of assumptions, and there are no systematic criteria for selection, resulting in wide ranges of estimates. Some of the reported large estimates are difficult to implement in practice. The most influential assumption, which is also highly variable, and probably the most controversial is the future role of dedicated bioenergy crops—their yields prediction, water and land availability for their production, level of deployment that might be achievable in practice, and their sustainability assurance.

The globally available biomass for energy cannot be measured directly; it can only be modelled based on various existing databases such as Food and Agricultural organization (FAO) databases, satellite image data, field trials, current and future predicted energy, food, timber and demands for other land based products. All models aim to integrate information from these sources to predict the future role of biomass, but they vary in complexity and sophistication. The future supply of biomass depends on the availability of land for energy crops, food, feed, and timber products, and also anticipated future economic activities which might require land. Other factors which will influence land availability include production technological improvement, population growth, and environmental constraints such as water, nutrients, soil degradation and climate change (Thrian et al. 2011). Most biomass estimates target year 2050, reflecting the importance of this date in climate mitigation strategies. Using the available literature in 2007 and additional modeling (Dornburg et al. 2008, 2010) estimated the technical biomass potential in 2050 to be up to 500 EJ yr^{-1}. Their study assumed a policy framework that secures good governance of land use, and major improvements in agricultural management. It also takes into consideration the water limitations, biodiversity protection, land degradation, and competition with food. Other assessments have reported the technical biomass potential as high as 1000 EJ yr^{-1} (Smeets et al. 2007; Hoogwijk et al. 2005). The discrepancies are generally the result of differing assumptions on the future yields of food and energy crops, feed conversion efficiencies, and also the suitability and availability of land for dedicated energy crop production (Haberl et al. 2010).

Three major categories of biomass for energy production are: residues from agriculture and forestry, organic wastes and surplus forestry biomass, and dedicated energy crops. Dedicated energy crops are generally projected to make up most of the potential bioenergy production. Its potential ranges from 0 to 810 EJ yr^{-1} (Table 12.4). However, their large-scale cultivation is also the most controversial aspects of bioenergy production. In contrast, agricultural residues and waste materials are considered to be more sustainable because they have fewer direct impacts on land use and competition with food crops, but also agricultural residues are also required for maintaining soil organic matter and prevent soil erosion (Lal 2010) while in forests, detritus supports important elements of ecosystem and its removal may lead to depletion of nutrients pools essential for long-term soil fertility, production, and plant growth (Akselsson et al. 2007). Organic residues and wastes—including crop residues, animal manures, and municipal biosolid waste (MSW) represent a significant global bioenergy source. Its rational utilization produces energy cost-effectively while also minimizing environmental impacts from their alternative disposal methods—such as landfill and burning. Estimated global potential recoverable crop residue, based on 0.5–0.75 recovery of both primary (field) residues in 2050 ranges from 38 to 41 EJ yr^{-I} (Hakala et al. 2009) and secondary (processing) residue at 16 EJ yr^{-1} (Smeets et al. 2007). Other reports estimated technical potential from crop residues ranges of 46–66 EJ yr^{-1} (Smeets et al. 2007). Global technical potential of recoverable MSW has been estimated at 17 EJ yr^{-1} (Smeets et al. 2007), while the energy equivalent of recoverable manures through biogas potential is estimated at 25 EJ yr^{-1} (Johansson et al. 1992) and 9–39 EJ yr^{-1} (Haberl et al. 2010). Therefore, the residues from agriculture, forestry, and organic wastes from municipal solid waste, animal dung, and process residues is estimated at 40–170 EJ yr^{-1}. Surplus forestry other than forestry residues were estimated at 60–100 EJ yr^{-1} (Chum et al. 2011).

Studies on global technical bioenergy potential suggest that plants cultivated specifically for energy represent the largest component of future bioenergy production. A variety of plants can be grown for this purpose including—poplar, willow, eucalyptus, miscanthus *(Miscanthus* × *giganteus)*, switchgrass (*Panicum virgatum*), oil crops such as rape seed, sunflower, hemp, jatropha (*Jatropha curcas*); sugar crops such as sugar cane, energy cane; starch crops such as cereals (de Wit and Faaij 2010; Sims et al. 2006; Bauen et al. 2009; WBGU 2009). Yield expectations from bioenergy crops differ widely ranging from 6.9 to 60 MJ m^2 yr^{-1} (Table 12.3). The discrepancies arise from both assumed type of land available for bioenergy, water resources, energy crop type and level of nutrient input assumptions (Smeets et al. 2007; Marland 2008). Most studies do not identify specific energy crop species but assume that the best adapted crop foe the available land type will be used. The projected area available for bioenergy crops range from 0.6×10^6 to 37×10^6 km^2 (Table 12.3), which is 0.4–28% of the Earth's land except Greenland and Antarctica (Table 12.2). The discrepancies between different studies is mainly the result of different assumptions on constraints, such as area requirement for food, fiber, and pasture; water availability, biodiversity protection, urban and infrastructure requirements (Haberl et al. 2010), soil and climatic factors, projected future crop yields, and other societal factors determining future food preference and demand.

The biomass produced from energy crops produced from surplus arable and pasture lands was estimated at 120 EJ yr^{-1}, and an additional 70 EJ yr^{-1} from water-scarce marginal and degraded lands (Dornburg et al. 2010). The main assumption for the estimate is that the arable land available for bioenergy crop production is limited due to high demand for food and limited gains in land productivity. Therefore, the energy crop production will mostly come from abandoned agricultural lands, deforested and degraded lands and limited expansion of energy crop onto pasture lands. By using extrapolation of regionally specific biomass input and output ratios of livestock and dietary assumptions, (Erb et al. 2009) observed that 2.3–9.9 million km^2 may become available in 2050 for bioenergy crop plantations if the most suitable grazing areas were intensified as much as possible (Erb et al. 2009). Land requirement for food crop production is strongly influenced by yield projection for cereal crops, because two-thirds of all energy in human diets is provided by three crops—wheat, rice and maize (Cassman 1999) and their production occupies 10% of global land area. IMAGE model calculations which took into consideration the constraints such as soil degradation and water scarcity estimated global dedicated bioenergy crop reductions ranging from 65 to 148 EJ yr^{-1} in 2050 (van Vuuren et al. 2009). Several studies (Hoogwijk et al. 2005, 2009) estimated that biomass potential could expand from 290–320 EJ yr^{-1} in year 2020 to 330–400 EJ yr^{-1} in year 2030. Their higher estimates assume that in addition to abandoned farmland, deforested and degraded land, a limited good quality agricultural land will be spared for energy crop production. These estimates also assume that increase in crop yields will keep pace with anticipated population growth. Table 12.3 presents the global bioenergy crop production technical potential based on the surveyed literature. However, achieving the technical potential will require major policy efforts. Therefore, the actual deployment may be lower than estimated technical potential.

Summarized ranges of global potential of different types of biomass by the year 2050 are presented in Table 12.4. The wide ranges of the reported values are the

Table 12.3 Global estimates of bioenergy potentials from dedicated crops by the year 2050

Land category	Estimated area (km^2 × 10^6)	Estimated yield (MJ m^{-2} yr^{-1})	Global bioenergy potential (EJ yr^{-1})	Reference
Abandoned farmland	3.9–4.7	8.2–8.7	32–41	Campbell et al. (2008)
	3.9	6.9	27	Field et al. (2008)
Abandoned farmland and farmland	2.5–5.2	14–23	34–120	WBGU (2009)
	<6	19–60	65–300	van Vuuren et al. (2009)
	27–37	10–18	300–600	Hoogwijk et al. (2005)
Surplus farmland and pastureland	7.3–35	29–39	215–1272	Smeets et al. (2007)
	na	na	120–330	Dornburg et al. (2010)
Surplus and marginal land	na	na	60–810	Bauen et al. (2009)
Sustainable energy crops	na	na	190–330	
Energy crops	3.9–35	6.9–60	27–810	

Table 12.4 Potential for global sustainable land-based biomass potential for bioenergy

Biomass type	2050 sustainable potential (EJ yr^{-1})	Comments
Agricultural residues	15–70	Residues from crop/fodder production and processing including corn stover, cobs, cereal straw, husks
Dedicated energy crops production from surplus arable land	0–700	Includes surplus agricultural crops, and dedicated energy crops—lignocellulosic perennial grasses, short rotation coppice tree plantations. Only arable land not required for food and fodder or other agriculture commodities is assumed available. High potential requires global development of high yielding agricultural production. Zero potential reflects the lack of surplus agricultural land
Dedicated energy crops production from marginal lands	0–110	Biomass production from deforested and degraded marginal lands that is unsuitable for conventional agriculture but suitable for some bioenergy farming (i.e., reforestation). Zero potential reflects low potential for these lands due to extensive management, therefore, poor economic performance
Forest biomass	5–50	Includes forest sector byproducts—primary residues from forestry thinning and logging, secondary residues such as saw dust, bark from wood processing, dead wood from natural disturbances—including fire, insect outbreaks, and biomass growth from natural and semi-natural forests that is not required for industrial roundwood products to meet projected biomaterials demand
Animal dung	5–50	Animal manure. Population and diets and character of animal production system are the critical determinants of the availability
Organic waste	5–50	Biomass from materials use, household organic waste, discarded wood products including papers, construction and demolition wood. Availability depends on competing uses and implementation of collection scheme
Total	50–1000	

Source IPCC (2012)

result of large uncertainties of factors determining the availability of the biomass—such as population, economic and technology development assumed in computing these potential, nature conservation, social preferences, the magnitude and patterns of climate change, and land use. All these factors can influence biophysical capacity of the environment to support the biomass availability. The data suggest that substantial supplies will come from dedicated biomass plantations. The underlying assumption behind significantly larger role of dedicated bioenergy crops contribution are (i) opportunity to increase crop yields and close the gap between the expected yields at optimum agronomic practices and the actual yields realized by farmers, (ii) agricultural intensification (Slade et al. 2014). As a result, arable cropland and pasture land will be spared from food production and made available for biomass production. However, bioenergy production estimates that are contingent on land sparing remains uncertain—mostly due to uncertain future climate, dietary changes, and population increase.

12.7 Classification of Biofuels

Generally, the classification of biofuels is related to the method of preparation, which in turn is related to starting feedstock that is converted to biofuels. For convenience, biofuels are generally classified as first and second generation depending on whether the conversion is based on simple sugars or more complex lignocelluloses as the energy source. First generation biofuels are those produced from biomass which is often a direct part of human food chain. They are considered conventional since they are produced from well-known process. Such fuels include, for example, the alcohol fuels that are made from fermentation and distillation of sugars, biodiesel made from esterification of edible oils, and biogas made from anaerobic fermentation of various biological wastes. Second generation biofuels are made from lignocellulosic feedstock which require more complex processes. There is also a third generation biofuels, sometimes referred to as advanced biofuels. These are produced from microalgae, seaweeds, and micro bacteria which are at research stage. Hydrogen as an energy carrier is also considered as an advanced biofuel. The second and third generation biofuels are not commercially available in the markets, since they require more complex process which is currently not economically viable.

12.7.1 First Generation Biofuels

The first generation biofuels are those produced from edible feedstock from agriculture sector—carbohydrates (grains and sugar), and oil seeds [rapeseed (*Brassica napus*), soybeans, peanuts (*Arachis hyopgea*)]. These feedstocks are often a direct part of food chain, and are converted to biofuels through conventional technologies. Their production processing are mature, well known, and commercialized (Arifeen et al. 2007). Commercial markets for their use in road transport are also in place (Sims et al. 2010). There are no major cost saving or increased efficiency technological breakthrough expected that would lead to large differences in terms of energy efficiency. Conventional crops feedstock are produced for human consumption and animal feed. Therefore, it might not be feasible to tremendously increase biofuel production to fulfil the desire for energy independence and mitigate CO_2 emission increase based on current 1st generation feedstock. The mature commercial markets for their road transport applications are currently in place. Currently the three most popular edible feedstocks that are exploited for biofuel production are sugar cane (in Brazil for bioethanol), corn (in the United States for bioethanol) and rapeseed (in various countries under European Union for biodiesel) (Fig. 12.4). Other feedstock are wheat (*Triticum aestivum* L) and sugar beet (EU); wheat and corn grain (China and Canada) (Balat and Balat 2009). Bioethanol is mainly blended in gasoline as a substitute to generate reformulated ethanol-gasoline mixtures. While the use of edible feedstock content may potentially enhance the conversion process and yield of biofuels, it tends to impact food prices (Cherubini 2010). The 1st generation of biofuels currently in the market are: (i) Bioethanol produced exclusively from the hydrolysis and fermentation of cereal starch or fermentation of sugars from sugar cane or sugar beet (*Beta vulgaris* L.) (Gomez et al. 2008); (ii) Biodiesel made from oil crops such as soya bean (*Glycine max* L, Merr), palm oil (*Elearis guineansis* Jacq), canola, rapeseed oil, and animal fat after conversion to fatty acids and methyl or ethyl ester through esterification process, and (iii) biogas also known as biomethane or landfill gas produced by anaerobic fermentation of organic wastes, including animal manures. This can be scrubbed to produce high quality methane-rich fuel similar to natural gas.

Cereal grains and cultivated crops such as corn (maize), wheat, sorghum, cassava, and potatoes possess a high starch content which can be obtained in high yields if cultivated properly. Corn is the largest fuel crop producing bioethanol and one of the most important agricultural crops globally, mainly because it utilizes a highly efficient C_4 photosynthesis pathway for C fixation. In contrast to C_3 photosynthesis pathway for most plants, C_4 photosynthesis pathway yields a higher starch content. The global production of corn grain is estimated at 0.822 Pg (Petagram = 10^9 kg) and major producers of corn are USA, China, and southern Africa nations. Numerous desirable traits have been enhanced through breeding and genetic modifications over the years to increase and optimize grain production (Torney et al. 2007). While wheat and rice are also important grains with high starch content, their use for biofuel production is currently not as common as these crops are harvested primarily for human food consumption. Two other important crops that may potentially be used for biofuel production are cassava and sorghum. Cassava (*Manihot esculenta*) is perennial root crop cultivated as annual crop in tropical and subtropical countries. The largest producers currently are Southeast Asia and various African countries. It also possesses high starch content and is recognized as an alternative to corn and sugar cane for the production of bioethanol (Worldwatch Institute 2007). Although the cassava ethanol production system is compatible with current corn ethanol technologies and infrastructures, the cassava cultivation is more labor intensive and the ethanol yield obtained from cassava is substantially lower than those from sugarcane and corn (Worldwatch Institute

2007). Sorghum is cultivated in temperate to hot and dry climates, and is the most widely grown cereal crop globally. It has ~30 species which provide human food, animal feed and forages, and sugar. As a C_4 plant, it has a high grain yield, starch, and biomass content, and is currently being developed as a potential bioenergy crop (Rooney et al. 2007). Its conversion process for bioethanol depends on type and part of sorghum to be used, however. The properties of sorghum are also currently being improved by breeding and genetic engineering approaches for biofuel feedstock (Saballos 2008).

Sugarcane is a perennial grass cultivated in the tropics and subtropics. Global production is estimated at ~1740 Gg. the largest producer of sugarcane is Brazil, other countries include Australia, India, South Africa and Thailand (Worldwatch Institute 2007). As a C_4 plant with fast growing rate, high sucrose content (~20%), it becomes preeminent choice for biofuel production, and is currently supplying ~40% of all fuel ethanol globally. Brazil has developed a green sustainable sugarcane ethanol industry, mainly due to its vast arable land, cheap feedstock price, and advanced agricultural technologies. Stem cutting has been the reproduction method for propagation. Stems are also milled for juice extraction, followed by biorefinery process to produce bioethanol (El Bassam 2010). The byproducts and residues of bagasse and molasses from sugarcane milling process are also important in ethanol fermentation and power generation, making the net energy ratio of sugarcane relatively higher than that of corn ethanol. Other alternatives to sugarcane are beet and sweet sorghums. However, due to lower harvestable yields and labor intensive cultivation schemes, these crops are not currently utilized for biofuel (El Bassam 2010).

Oilseed crops such as rapeseed, soybean, sunflower, peanut, palm, coconut safflower, linseed, and hemp are used as valuable feedstock for the production of liquid biofuels (Murphy 2012). These oils are also used for culinary purposes and for deriving other commodities—including soap, skin care products, and perfumes. The vegetable oils produced from these crops can be directly used in conventional or modified diesel engines or refined by transesterification with a short chain alcohol to produce alkyl esters (methyl, ethyl or propyl esters) commonly named as biodiesels (Shahid and Jamal 2011; Juan et al. 2011). Oilseed crops typically generate lower yield per unit area than sugar and starch crops in temperate regions, and therefore, expensive to produce. However, oilseeds require less processing, and therefore, have generally positive global energy balance per unit of feedstock. Oilseeds grown in tropical areas tend to be more productive and more competitive.

Biogas is obtained as landfill gas or produced by anaerobic fermentation (i.e., digesters) of organic wastes and animal manures. Biogas produced from landfills or digesters can be treated to remove inert gases such as CO_2 and N_2 and other contaminants such as hydrogen sulfide (H_2S), sulfur compounds, and siloxanes to varying levels before it is injected into commercial distribution pipeline. Biogas can also be purified to produce high quality methane rich fuel and compressed natural gas (CNG) (Sims et al. 2008).

The sustainable and economic production of 1st generation biofuels has come under close scrutiny. Their potential to meet liquid transport fuel targets set by various government mandates and policies globally and help achieving the goals of fossil fuel substitution, economic growth and climate change mitigation are limited by three main factors among others: (a) competition for land and water resources used for food, feed, and fiber production (Fargione et al. 2008b; Searchinger et al. 2008), (b) high production and processing costs which often require government subsidies in order to compete with petroleum fuels (Sims et al. 2010), and (c) widely varying assessments of the net GHG reductions once direct and indirect land use change is taken into account (OECD 2008). However, including direct and indirect land use change in lifecycle analysis is not always possible due to inadequate data. Other limitations include: (i) marginal GHG emission reduction benefits, with the exception of sugar cane ethanol and landfill gas, (ii) environmentally unsustainable production (Bonin and Lal 2012), (iii) accelerated deforestation (Fargione et al. 2008b), (iv) potential for negative impacts to biodiversity (Bonin and Lal 2012), and (v) competition for scarce water resources in many drier regions (Fargione et al. 2008b; Sims et al. 2008; Searchinger et al. 2008).

Many analyses in current literature indicate that the majority of 1st generation biofuels have no significant benefits in terms of GHG emission reductions and energy balance (Hill et al. 2006; Adler et al. 2007; Fargione et al. 2008b; Davis et al. 2009). For example, ethanol produced from corn grains reduces GHG emissions by only 12% compared to fossil displaced (Hill et al. 2006). It is also argued that first generation biofuels may actually produce more CO_2 emissions than fossil fuel they replace, when factoring emission due to land use changes and conversion of natural habitats into cropland which releases CO_2 sequestered in trees, grasses and soils (Searchinger et al. 2008), but these estimates have been debated (Mathews and Tan 2009). Even though crops grown for bioenergy production purposes are currently estimated to occupy only 2% of world's arable land (Sims et al. 2010), many authorities agree that 1st generation biofuels have contributed to the price increase of world commodity food and animal feed, at least in part, although much uncertainty exist in this regard. Estimates of biofuel contribution ranging from 15 to 25% of the total food price increase are suggested, with others at virtually zero, and still others as high as 75% (Naylor et al. 2007; Keyzer et al. 2008). The recent food commodity price decline without any reduction in biofuel production has been used to reinforce the view that biofuels were not the major reason for recent food prices increase. Regardless of the degree of certainty, competition with food and feed will remain an issue as long as 1st generation biofuels produced from food crops dominates the biofuel production.

12.7.1.1 Biodiesel

Biodiesel is a diesel replacement fuel for use in diesel engines. It is manufactured from plant oils or animal fats and various combinations of these feedstocks (refer Sects. "Feedstock" and "Biodiesel Production"). It refers to processed edible plant oils and/or animal fats. Raw or refined vegetable oils that has not been processed into biodiesel such as straight vegetable oils (SVOs) are not biodiesels, and they create engine problems when used as diesel fuels in direct injection engines and therefore, they should be avoided (DOE 2016a). Their high viscosity, lower volatility, and the reactivity of saturated hydrocarbon chains cause coking and impacts the injectors by causing poor atomization, ultimately leading to operational problems including engine deposits (Ma and Hanna 1999; Lang et al. 2001). Because of subsequent problems such as C deposits in the engine, engine durability, and lubricating oil contamination, they must be chemically transformed to be compatible with diesel engines specifications and be able to be used on a long-term with existing engines (Ma and Hanna 1999). There are four possible solutions which have been proposed to reduce the viscosity: trans-esterification pyrolysis dilution with petroleum-based fuel, and emulsification (Schwab et al. 1987). Trans-esterification is a common method which produces mono alkyl esters of long chain fatty acids or fatty acids alkyl esters. The idea of esterification originated in 1938, when it was realized that glycerin had no calorific value and likely causes excessive C deposit on the engine, therefore it should be eliminated from the vegetable oils to enable engine to run on the residue fatty acid (Walton 1938). The residue fatty acid is what is generally known as biodiesel today. Saturated fatty acids are more compactable, and their content enhances the oil energy density. However, if the oil or fat contain too much saturated fatty acids, they become solid at room temperature and cannot be directly used as fuel in diesel engine in their original form, except in warm climates. Biodiesel is mono alkyl esters of long chain fatty acids that are prepared from acyl-glycerol (triglyceride) in vegetable oils through trans-esterification with short chain alcohols. The oil and fats contain a mixture of triglycerides, free fatty acids, phospholipids, sterols, water, odorants and other impurities.

Biodiesel is simple and effective, it is miscible with petroleum based diesel fuel in all proportions, and can be used as fuel either in pure biodiesel or blended with petroleum-based diesel (Knothe and Krahl 2005). There are as many different biodiesels with different oil compositions. Oilseed species differ considerably in their saturation and fatty acid content, the main characteristic that significantly affect the properties of the biodiesel produced. The boiling and melting points of fatty acids, methyl esters, and glycerides increase with the number of C atoms in the chain, but decrease with increasing numbers of double bonds (Ma and Hanna 1999). The most commonly used biodiesels are fatty acid methyl esters (FAME) produced from plant oils combined with methanol through transesterification (i.e., transforming esters). Transesterification is carried out in the presence of homogenous and heterogeneous catalysts which produces FAME and glycerol, which is a high value co-product of biodiesel production. In addition to trans-esterification of triacyl-glycerol (TAG), biodiesel can be produced from free fatty acid through esterification (forming esters). The two other conversion routes, micro emulsion and pyrolysis are not economically viable. Pyrolysis is expensive for modest throughput and processing removes any environmental benefits of using a biofuel (Ma and Hanna 1999). Trans-esterification is alkali catalyzed reaction that requires 107.5 kg of methanol per Mg (ton) of vegetable oil, and results in production of 1004.5 kg of methyl ester and 103 kg of glycerol (Graboski and McCormick 1998). In this three-step reaction, triglycerides are converted into di-glycerides, then mono-glycerides and finally reduced fatty acid esters, thereby enhancing the viscosity of the final biodiesel.

The viscosity of vegetable oils and that of their final esters is of the order of 10–20 times and twice that of diesel fuel, respectively (Lang et al. 2001). The pre-step and catalysts make it possible to deal with the impurities such as free fatty acids and water to improve the reaction kinetics (Ma and Hanna 1999). Methanol is preferred over ethanol because of its physical and chemical properties as well as comparable low cost (Ma and Hanna 1999; Lang et al. 2001). However, it introduces part of fossil fuel into the biodiesel. For different esters from the same vegetable oil, methyl esters may also to be most volatile (Lang et al. 2001).

When biodiesel displaces petroleum diesel, it significantly reduces life-cycle GHG emissions. For example, complete lifecycle analysis conducted by Argonne National Laboratory indicated that GHG emissions for B100 biodiesel is 74% lower than those from petroleum diesel, and also similar values have been reported for its lifecycle analysis from various sources (CARB 2015). In addition, biodiesel used as additive to diesel fuel can improve its lubricity. This property is becoming increasingly valuable as recent legislation has mandated further regulation on the sulfur content of diesel fuels. These cleaner diesel fuels exhibit reduced lubricity as compared with high sulfur predecessors (Radich 2004; Goodrum and Geller 2005). Some fatty acids such as ricinoleic (from castor oil) and lesquerolic acids (from *Lesquerella* spp) could be especially efficient in enhancing the lubricity of diesel fuel to an acceptable level at concentrations as low as 0.25% (Goodrum and Geller 2005). Biodiesel is also fully compatible with the emission control catalysts and filters that are used to reduce nitrogen oxides (NO_x) and particulate matter (PM) emissions from new diesel engines (Lammert et al. 2012).

Blending biodiesel with diesel fuel can also increase the neat cetane number. Cetane number increases with increasing length of both fatty acid chain and ester group, while it is inversely related to the number of double bonds, and as double bonds and carbonyl groups move towards the center of the chain (Graboski and McCormick 1998; Task Force 2007). Highly saturated oils with low number of double bonds, therefore, provides the fuel with superior oxidative stability and higher cetane number. The average cetane numbers are 50.9 for soy and 52.9 for rapeseed esters. For the other esters the range is 48–60 (Graboski and McCormick 1998). In comparison, the cetane index for petroleum diesel ranges from 40 to 52 (Radich 2004). Blends of B20 or lower (i.e., 20 biodiesel units to 80 units of petroleum diesel) require no new equipment or equipment modifications. Similarly B20 can be stored in diesel tanks and pumped with the same equipment as diesel fuel. However, B20 does present few unique handling and use precautions even though most users can expect trouble-free B20 experience.

The co-products of the biodiesel processing chain are meal left in the seed extraction, which is sold as animal feed; and the glycerin from glycerol recovery, used in cosmetics. However, the rapid expansion of biodiesel has already saturated the market for glycerin in Europe, undercutting its ability to reduce the biodiesel price as it could offset 5% of production cost.

Feedstock

The feedstock for biodiesel production can be categorized as any lipid source. The lipid feedstock includes vegetable oils from a large range of oilseed crops, mainly—rapeseed, canola, soybean, corn, and sunflower (*Helianthus annuus*), or palm oil, and jatropha (*Jatropha curcas*) in tropical climates. Other potential plant oil feedstock includes mustard seed, linseed, castor oil, peanut, cottonseed, coconut, *Lesquerrella* spp, jatropha, and microalgae. Other feedstocks include recycled cooking greases or oils (e.g., yellow grease), or animal fats (beef, tallow, pork, lard) and various combinations of these feedstocks. Used cooking oils are mostly plant-based, but may also contain animal fats. Used cooking oils are both recycled and renewable. As biodiesel production and use increases, new feedstocks are also been developed and may soon be introduced to the market. Such examples include pennycress, camelina, cuphea, brown grease, and various strains of algae (DOE 2016a). Although there is little biodiesel currently available from these new feedstocks, great potential exist for these new feedstocks to supplement the current feedstock supply.

Rapeseed is currently a common feedstock in European Union (EU) countries and Canada, while soybean oil is common feedstock in the United States. Palm oil is common feedstock in tropical countries such as Indonesia, Malaysia. Jatropha oil and karanja oil (*Pongamia pinnata*) is common non-edible oils used as lipid source in India. The major difference between various vegetable oils is the type of fatty acids attached in the triglyceride molecule. Fatty acid composition determines fuel properties of biodiesel derived from corresponding vegetable oils (Ramos et al. 2009). Fatty acid composition also determines the degree of saturation or unsaturation and molecular weight of vegetable oils.

Biodiesel Production

Biodiesel is a renewable fuel that can be manufactured from new and used vegetable oils, animal fats, and recycled restaurant grease. Its physical properties are similar to those of petroleum diesel, but it is cleaner-burning renewable alternative, and using biodiesel in place of petroleum diesel reduces lifecycle C emissions, while also reducing emissions of toxic air pollutants in older on-road vehicles and many off-road applications. The biodiesel manufacturing process converts oils and fats into chemicals called long-chain mono alkyl esters through a process referred to as esterification. Generally, 100 units of oil or fat are reacted with 10 units of short-chain alcohol (usually methanol) in the presence of a catalyst (usually sodium hydroxide (NaOH) or potassium hydroxide (KOH) to form 100 units of biodiesel and 10 units of glycerin or (glycerol) as a co-product of biodiesel process (Eq. 12.1):

$$\text{Oil} + \text{alcohol} \rightarrow \text{biodiesel} + \text{glycerin} \tag{12.1}$$

For biodiesel to be sold in the market, the fuel must meet certain quality specifications. In the United States, biodiesel must meet the American Society for

Testing and Materials (ASTM) requirements for biodiesel fuel. The ASTM D6751 definition of biodiesel states that biodiesel is composed of "mono-alkyl esters of long-chain fatty acids derived from plant oils or animal fats" (DOE 2016a), where mono-alkyl esters indicate that biodiesel contains only one ester linkage in each molecule. Raw or refined plant oils, animal fats, and greases contains three ester linkages and are therefore, not legally biodiesel. Biodiesel can be made from methyl, ethyl, isopropyl, and other alcohols, but virtually all commercial biodiesel production in the US currently is based on methyl esters, mainly due to higher ethanol prices relative to methanol, lower ethyl ester conversions, and the difficulty of recycling excess ethanol from finished biodiesel which has hampered ethyl ester production in the marketplace (DOE 2016a). Biodiesel differs from renewable diesel in that renewable diesel is a hydrocarbon diesel fuel produced from renewable feedstocks. Currently, like biodiesel, all renewable diesel on the market is produced from fats and oils, but the way these fatty acids are reacted into fuels is the main defining difference between biodiesel and renewable diesel. Renewable diesel is produced by hydroprocessing of fats and oils. Hydroprocessing produces alkanes, which are chemically identical to some compounds found in conventional diesel fuel from petroleum. The properties of renewable diesel are also different from biodiesel in that it has very high cetane number and a cloud point more like conventional diesel fuels. However, some similarities between biodiesel and renewable diesel exist, which include near-zero aromatic content, and very low sulfur content (DOE 2016a).

12.7.1.2 Bioethanol

Bioethanol, bioalcohol or ethyl alcohol (C_2H_5OH) is the most commonly utilized biofuels, which are produced from the fermentation of sugars by various enzymes and microorganisms, followed by distillation. It is a single compound biofuel whose final composition does not vary with the type of feedstock used. The feedstock can vary from sugarcane, sugar beet, starch crops such as corn, wheat, sorghum, potatoes, cassava and any other saccharide source from which simple sugars can be obtained by hydrolysis (Fig. 12.5). Starch is processed through pretreatment and hydrolysis, then the resultant sugars are basically equally processed through fermentation by yeasts and other microbes and distillation. The process of bioethanol production relies on the metabolism by yeasts (mostly *Saccharomyces cerevisiae*) that are able to turn sugars into ethanol.

The main sugar-containing crops are sugar cane and sugar beet. Sweet sorghum could also become interesting ethanol feedstock as a multiuse crop whose seeds are edible and stalks contains sugar. The main starch crops used nowadays are corn and wheat, potatoes, cassava, and sorghum grains to a less extent. Sugar crops typically yield higher amount of sugar per unit area compared to starch crops. Sugar can also be directly fermented, while starch long polymers have to be hydrolyzed before being fed to yeasts for the fermentation process. Saccharification converts high molecular weight polymers of starch to short oligomers and finally to monomers of

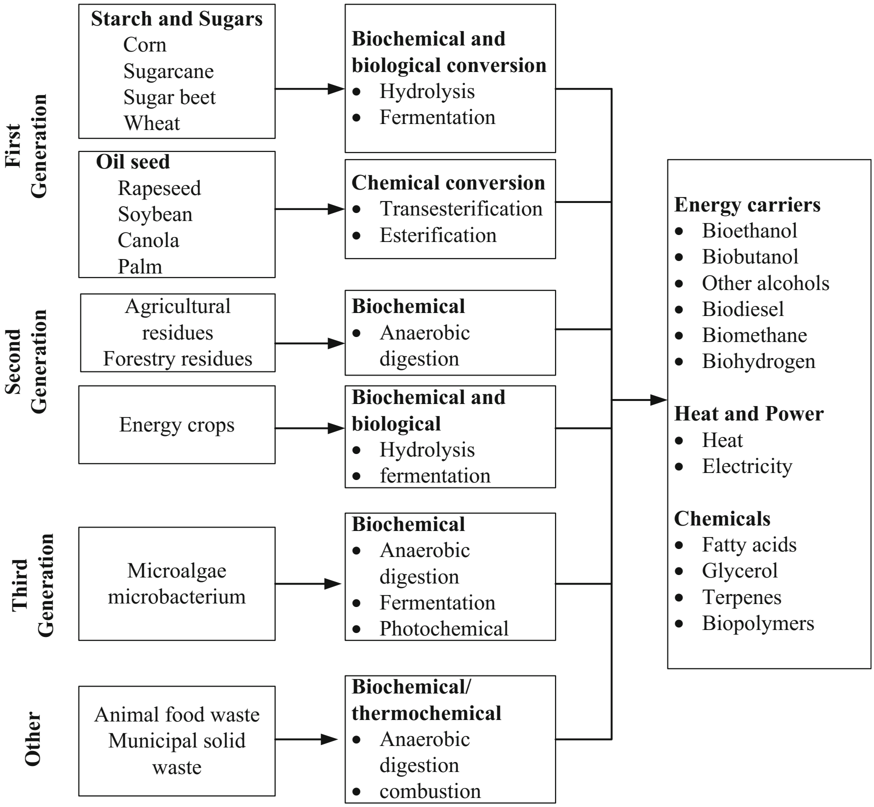

Fig. 12.5 Biomass feedstock for biofuel production, current conversion processes, final energy carriers and biorefinery products produced

glucose (Arifeen et al. 2007). Starch are homogenous polymer of glucoses linked by α-1,4-glucosidic bonds, composing both linear (amylose) and branched (amylopectin) forms in its structure. The molecular arrangements of α-1,4 bonds gives starch helical structure, and α-1,6-glucosidic linkages of amylopectin causes branches (Smith 2001), which results in loosely-packed amorphous structures that are easy for weak chemicals or enzymes to hydrolyze.

Starchy crops are either processed through ‘wet milling’ or ‘dry milling’ at their entry in the processing chain. In wet milling, grains are soaked and chemically sub-divided into rich starchy parts of primary interest (i.e., grain endosperms) and the other parts that contain more protein and fibers and constitute diverse co-products (corn oil and syrup, gluten feed, germ meal, vitamins, and amino acids). These co-products can contribute up to 25% of the processing economy. The dry milling method only consists of grinding of the unprocessed heterogeneous seeds into granules. It is less expensive, but it also leads to less diverse co-products production.

Fermentation of sugars, regardless of their origin, is normally done using yeasts. Under idealized conditions, 0.51 g of ethanol per gram of hexose is produced (Busche et al. 1991). However, only about 95% of this value is achieved. The main co-product is the dried distiller's grain which is fed to animals that can digest high proportions of fibers, and this contribute up to 20% of the bioethanol processing economy. Through both dry and wet processes, the starch is finally hydrolyzed into sugar, typically using a high-temperature enzyme process (Fulton et al. 2004; Cardona and Sanchez 2007). The CO_2 from fermentation process can also be sold as a co-product to beverages industries. In a conventional fermentation process, approximately one-third of the C available in the sugar is lost as CO_2. The fermented ethanol must be distilled until enough water is removed to make the final anhydrous ethanol suitable for blending with gasoline (usually <1% water in temperate climates).

Bioethanol is a substitute for gasoline in internal combustion engines. Water in ethanol blended with gasoline makes the fuel more sensitive to frost and increases the risk of phase separation in both gasoline storage facilities and in the vehicle fuel tanks, which can cause serious operation problems for the gasoline engines (Balat et al. 2008). Phase separation due to water content occurs more readily at lower levels of ethanol in gasoline blends. In Brazil and US where ethanol blends reaches up to 20–25 and 5.7–10%, respectively, phase separation is not a major problem. However, it can be a major problem in Europe where ethanol content in gasoline is lower. To improve the ethanol quality in low blending percentage, ethanol (47% on a mass basis) can be converted into Ethyl-Tertio-Butyl-Ether (ETBE) by reaction with isobutylene (53%). An ETBE blend of 15% corresponds to a blend in volume of 7% ethanol. Therefore, bioethanol can be used as feedstock for making ETBE which blends more easily with gasoline.

12.7.1.3 Benefits of Biodiesel and Bioethanol as Blends in Liquid Fuel

Bioethanol has higher octane number (108), broader flammability limits, higher flame speed and higher heat of vaporization, the characters which allow for higher compression ratio and shorter burning time, and efficiency advantages over gasoline in an internal combustion engine (Balat 2007). Since they both contain oxygen, ethanol and biodiesel are both better combustibles than the substituted fossil oils, reducing the emission of pollutants such as CO, hydrocarbons, sulfur oxides, and particulates by up to half of these emissions depending on the biofuel and the blend mix (Shahid and Jamal 2008; Murugesan et al. 2009). Exhausts from blends with vegetable oils also depend on the engine and load (Murugesan et al. 2009).

For the NO_x emissions from biofuels, the conclusions are not unanimous, but biofuels may lead to slightly higher NO_x emissions (Graboski and McCormick 1998; Radich 2004), especially those blends with higher than 20% of ethanol or biodiesel in cars driven in the city. The NO_x emissions have been reported to be in the range of 10% higher compared to diesel in 2008 (Murugesan et al. 2009). Biofuels increases octane levels, due to ethanol (Harijan et al. 2009; Balat et al.

2008), and cetane number, mostly due to biodiesel (Radich 2004). Gasoline's high octane value indicates a smaller likelihood that the fuel combusts too soon (i.e., low auto-ignite tendency), provoking engine knock problems. A high tendency to auto-ignite or low octane rating is undesirable in spark ignition engine (gasoline) but desirable in a diesel engine (high cetane number). However, both ethanol and biodiesel may cause corrosion and are sensitive to cold weather.

The primary advantage of biofuels is the convenience that they can be used as blends with conventional fuels in existing vehicles, although they are limited to some extent, according to vehicle specifications. The blends are reported on volume basis. In US for example, the blends are 5 and 10% ethanol and in Europe 5% ethanol and 5% biodiesel. Beyond the current limits, engines have to be adopted so that their performances will not be affected in the long run. This is the case for the flexible-fuel vehicles that can run on low- and high-level ethanol blends—up to 85–100% (sold as E85, E90, or E100); biodiesels blends are denoted by B (i.e., B20, or B30). As more countries are accepting the biofuels, there is a need for standardization, in both engine specification and quality of the biofuels used in conventional fuel blends. However, it is more difficult to come up with a standardized measure due to biofuel feedstock variances worldwide, climatic conditions in each country and regions, and market characteristics.

12.7.1.4 Biogas

Biogas is a renewable energy which can be used for replacement of fossil fuels in power and heat generation and also as gaseous fuel for powering vehicles. It is produced through anaerobic digestion of biodegradable organic materials such as municipal solid wastes, liquid slurry, solid manure, corn silage, or other agricultural waste by bacteria. The process is sometimes termed as methanization, due to high concentration of methane in biogas. The more the dry matter content, the greater the biogas yields. Biogas contains substantial quantity of methane (CH_4) ranging between 55 and 70% and CO_2 (30–45%) and is saturated with water vapor (Weiland 2010). Other contents include small quantities of hydrogen sulfide (H_2S) ranging from 100 to 3000 ppm, and other trace gases such as ammonia. The separation of the other components of biogas using scrubber makes it an expensive prerequisite in order to use biogas as fuel or to mix it with natural gas. However, once scrubbed it is as good as natural gas. Removal of H_2S is a prerequisite for power generation or combined heat and power. Removal of H_2S is mainly done by biological desulfurization. Biogas has less appeal to transportation biofuel, and the target vehicle fleet remains marginal, mainly because of the onboard gas storage constraints.

The primary interest for biogas remains in local development as fuel for heat and power plants. Simple anaerobic digester technology can produce clean biogas fuel for cooking from animal manure, crop residues and other organic waste feedstocks. Biogas systems performs better in warmer climates, although they can function under a variety of conditions. Biogas is best suited for estimated 155 million households and commercial farms where sufficient animal manure and human waste can be collected on a daily basis (REN21 2014). However, domestic scale biogas installations have surged in some countries, driven in part by number of international programs. For example, China added 1.8 million units in 2013, bringing the total to 43.5 million units thereby remaining the global leader in the use of small-scale biogas plants. India added 125,000 units in 2012 bringing the total to nearly 4.7 million by 2013, while Nepal and Kenya had 290,500 and 9000 biogas units in use by 2013 (REN21 2014). In the USA, more than 2000 sites are producing biogas, and with proper support additional 11,000 biogas systems could be installed to produce enough energy to power 3 million American homes and reduce CH_4 emission by 4–54 tons by 2030 (USDA 2014). Production of biogas from biological wastes through anaerobic digestion is growing worldwide, and it is considered ideal in many ways because of its economic and environmental benefits. Other benefits offered by the use of biogas over natural gas include: (i) produced locally without dependency on foreign natural gas supply, (ii) reduces pollution by organic waste, and (iii) reduced waste management problems such as landfill needs. The European energy production from biogas reached 110 TJ (Terajoule = 10^{12} J) of heat and 44.5 GWh of electricity in 2012. The small reminder was upgraded to bio-methane and injected into national natural gas grid (REN21 2014). Currently, Germany is the largest biogas producing country in Europe with 4000 agricultural biogas production units on German farms (Weiland 2010). Chinese government has set a target of 45 million biogas digesters by the year 2020 (REN21 2014). Biogas production from specifically designed digesters is the most widespread technology. But capturing CH_4 from municipal landfill sites is a fairly developed technology. In US for example, capturing CH_4 emissions produced by landfills has made it possible to reduce methane emissions by nearly 50% over the years (Kram 2007).

Biogas Feedstock

All types of biomass which contains carbohydrates, proteins, fats, cellulose and hemicellulose as the main components can be used as substrates for biogas production. Strongly lignified organic substances such as wood are not suitable for biogas production, however, due to slow anaerobic decomposition. Historically, anaerobic digestion has mainly been associated with treatment of animal manures and sewage sludge from aerobic wastewater treatment plants. But currently, agricultural biogas plants add co-substrates such as crop harvest residues, organic wastes from agriculture related industries, food waste, and energy crop biomass contents for achieving higher biogas yields (Weiland 2010). The composition of biogas and CH_4 content depends on the feedstock type, digestion system and the retention time (Braun 2007).

Biochemical Process

The CH_4 fermentation is a complex process which is carried out by different consortia of microorganisms which are strict anaerobes such as *Bacteriocides*, *Clostridia*, and *Bifidobacteria* (Weiland 2010). Furthermore, some facultative anaerobes such as *Streptococci* and *Enterobacteriaceae* may also take part. Methane fermentation can be divided into four phases: hydrolysis, acidogenesis, acetogenesis/hydrogenation and methanization. The individual degradation steps are carried out by different consortia of microorganisms with syntrophic interrelation but different requirements on the environment (Angelidaki et al. 1993). Hydrolyzing and fermenting microorganisms breaks polymers and monomers to produce acetate, H_2 and volatile fatty acids, and excrete hydrolytic enzymes, e.g. cellullase, cellobiase, xylanase, amylase, lipase, and protease. A complex consortium of microorganisms participates in the hydrolysis and fermentation of organic material. Many microbial details of metabolic processes as well as the network in a methanogenic consortium is not well understood, but the current knowledge suggests that H_2 may be a limiting substrate for methanogens (Bagi et al. 2007). The fermentation process occurs in two stages: hydrolysis and degradation. Methane formation takes place within a very narrow pH interval—from 6.5 to 8.5, with optimum pH interval of 7.0–8.0. The pH increases through ammonia accumulation during protein degradation, while accumulation of fatty acids decreases the pH, and both inhibits CH_4 production process.

At the end of the degradation chain, two groups of methanogenic bacteria which are strict anaerobes and requires lower redox potential than most other anaerobic bacteria, produce CH_4 from acetate or H_2 and CO_2. Only few species are known to be able to degrade acetate into CH_4 and CO_2, e.g. *Methanosarcina barkeri*, *Metanococcus mazei*, and *Methanotrix soeh*ngenii, but all methanogenic bacteria are able to use H_2 to form CH_4 (Weiland 2010). The reaction takes several days to degrade 10–15% of the biodegradable material, but biogas collection offers the advantage of cheap feedstock, and decrease in CH_4 emissions. The anaerobic digestion process results in mineralization of organically bound nutrients, particularly N, and lowering of C:N ratio. The process increases N fertilization effect, and allows the integration of residues in fertilization plan with reduced application of mineral N fertilizers. The solid residues of the process can be dried and used as fertilizer and also as soil amendments.

Although the 1st generation feedstock are attractive options for biofuel production in terms easiness of production and processing of food crops into transport fuels, the feedstock supply for first generation biofuels is considered unsustainable. Feeding nearly 10 billion people by 2050 becomes the highest priority, even though the demand for renewable energy has increased exponentially worldwide in the past few years. Production of fuels from food crops grown for human consumptions has generated concerns due to: (i) rising food prices (ii) relatively low or no GHG emission mitigation benefit, some have even argued that some of first generation biofuels being promoted may result into net GHG increase compared to fossil fuels they replace, (iii) high cost of the marginal CO_2 emission abatement; (iv) the continuing need for significant government support and subsidies for them to remain economically viable and competitive in fuel market; (v) direct and indirect impacts on land use change associated with the expansion of arable land to meet both food for human consumption and fuel demand, and (vi) their impacts on biodiversity and environmental pollution associated with increased fertilizers and pesticides use. The direct competition with human food and animal feed, grain-based biofuel is increasingly becoming a moral issue, and forcing research efforts to focus on the utilization of lignocellulose for bioenergy. There is also increasing concerns of growing traditional food crops (e.g., corn) for biofuels production, since they require more nutrients, land, water, and energy (Pimentel et al. 2009) which may lead to increased GHG emissions. Also, the breeding program for the current grain crops is optimized for higher grain and nutrients for food.

Despite the negative impacts of 1st generation biofuels, they have played an important role of in establishing the infrastructure and policy drivers required for developing a sustainable renewable transport fuels both locally and in the international market place.

12.7.2 Second Generation Biofuels

Second generation biofuels are produced from plant biomass that is not necessarily a part of food chain. Their production relies on lignocellulosic biomass, including agriculture and forest residues, and dedicated energy crops that are non-edible. These are considered biofuel feedstock of choice in the long run which does not compete with human food. Plant biomass are generally considered as the most abundant and underutilized biological resources globally especially as energy resources (Naik et al. 2010). At its most basic, plant biomass can be burned to generate electricity and heat, but greater potential and higher efficiency could be achieved by processing it into liquid and gas biofuels. The current biofuels debate has pushed the use of nonfood feedstock under the spotlight with the commonly expressed hope that the second generation biofuels will soon become commercially available, at a large scale production, and at a cost competitive with petroleum based fuels and resolve some of the socioeconomic and environmental challenges posed by the with first generation biofuels and environmental challenges associated with the use of fossil fuels. In addition to greater GHG mitigation potential, it is generally recognized that 2nd generation biofuels have two major advantages over 1st generation biofuels. These are: (i) more positive energy balance, and (ii) better access to sustainable biomass feedstock all year round, which would keep the biorefinery operating and spread the overhead costs.

In general, 2nd generation feedstock can be categorized into three major groups—dedicated energy crops, organic residues—including crop and forest residues, and surplus forest products (Margeot et al. 2009; Balat 2011; Ghosh and Hallenbeck 2012). Crop residues, including corn stover and wheat straw are also being considered for feedstock in the cellulosic biofuels. However, agricultural byproducts can only satisfy a small proportion of the increasing demand for biofuels. Approximately 40 Mg ha^{-1} yr^{-1} of lignocellulosic residues are produced from croplands. Most of crop residues are required for nutrient recycling and sustainability of the agricultural land, but some of it might be underutilized. Crop residues are derived from various agricultural processes and can include corn cobs, corn stover, wheat straw, rice hulls, and cane bagasse. In many developing nations these are currently either combusted during land preparation, used as forages, combusted for heat and electricity generation or plowed back into croplands. Excessive removal of crop residues may cause land degradation and also impact the long-term land sustainability. In addition, due to logistics of collecting the crop residues, and issues associated to supply chain, the estimated crop residue potential may not be achieved (Sims et al. 2010). Other organic residues include woody waste such as forest thinning, byproduct of logging operations; sawmill processes, pulp and plywood factories and lumber industry. For forest byproducts, excessive thinning and logging residue removal may also reduce long-term forest productivity and also affect wildlife habitat. Low cost wood residues, waste from agricultural and forestry processing industry, municipal solid waste which is generally landfilled can also be used as lignocellulosic feedstock. Where these feedstock are available, it can be possible to produce biofuels with no additional land requirements, and also with no impacts on food, fiber, and feed (Sims et al. 2008, 2010). Therefore, realizing the potential benefits of lignocellulosic biofuels will require judicious land management decisions which should be supported by policies which advance long term sustainability of both land, biodiversity, and the global environment as we navigate into low-C economy. It is important that policies guiding the development of biofuel sector are developed with global view, knowing that decisions made by individual country or region may have a global implications. The importance of woody biomass has been recognized because of their high cellulose and hemicellulose composition (Demirbas 2001; Nitayavardhana and Khanal 2012).

In the long run, sustainable biofuels feedstock will be generated from dedicated perennial biomass crops for energy. Dedicated biomass crops are plants that are able to produce substantial biomass yields in a short period of time, even when grown on marginal lands with minimal inputs of fertilizers and pesticides. The desired merits for dedicated energy crops include: fast growth rate, high tolerance to various biotic and abiotic environmental stresses, high productivity, high energy content, and relatively easy to cultivate. Currently the following energy crops are receiving high interest: perennial C_4 grasses such as miscanthus and switchgrass as well as woody species—willow, poplar, and eucalyptus (El Bassam 2010). Short rotation and fast growing energy crops are excellent feedstock due to their superior growth on wide range of environments and high biomass yields which minimizes competition for arable land. Additionally, energy crops have several advantages compared to food crops and agricultural residues: (i) perenniality eliminates the need for annual tillage and most chemical after the establishment phase, (ii) perennial crops also have the potential for SOC sequestration, (iii) energy crops also minimize the fertilizer N inputs which protect groundwater and surface water from nitrate leaching and pollution and reduce N_2O emissions, (iv) perennial grasses can also be grown as complex mixes for additional conservation benefits (Tilman et al. 2006), and (v) perennial energy crops provide the surrounding landscapes the biodiversity-based ecosystem services including pollination and pest suppression, while also providing higher rates of energy return and CO_2 emission mitigation than grain-based systems, and (vi) feedstock can be produced from marginal lands and degraded lands with fewer inputs which can reduce GHG emissions and energy requirements (Debolt et al. 2009). This will avoid competition with food and fiber and resultant effects on food and commodity price fluctuations.

12.7.2.1 Land Availability for Bioenergy Crops

One of the main constraints to expanding biofuel production is the limited amount of land available for producing biomass for energy. Since many regions are already experiencing pressure on land needed for critical socioeconomic activities, converting the existing croplands or developing new land for biofuel production raises concerns of food versus fuel debate (Service 2007), increased GHG emissions (Searchinger et al. 2008), and introduction of invasive species into existing ecosystems (Ditomaso et al. 2010). Current corn production alone may not be able to support the increase in demand for bioenergy feedstock without significant long-term impact on the arable lands. As it has been indicated in many studies, removal of crop residues from annual grain fields for use as biofuel feedstock reduces soil health and quality and land productivity in the long term due to decrease in nutrient recycling. It may also increase water and wind soil erosion risks and also cause soil compaction (Blanco-Canqui 2010; Meki et al. 2013). The extent of the impact on soil properties depends on soil characteristics, topography, tillage system, crop type, management, and climate, however. Residue removal also removes essential nutrients associated with residues which can impact nutrient use and management in the long-run (Fixen 2007; Hoskinson et al. 2007). In addition, increased fertilizer N and P nutrients application to sustain higher yields will lead to groundwater and stream pollution due to excessive N and P leaching (Christian and Riche 1998; Meki et al. 2013).

The increased bioenergy markets may become financial incentive to either convert existing croplands to grow dedicated energy crops, which may lead to indirect land use change for the displaced crop and livestock production or cause direct land use change by moving into forest and livestock production lands. One of the pressing question is what types of the land can be used for sustainable biofuel production, where are the lands, how much is available and what is the land currently used for? The answers to these questions are needed to provide the basis for justification of the potential of biofuel and form the basis for evaluating the associated long-term environmental and economic impacts of biofuel production.

Fast growing perennial grasses have higher water use efficiency; therefore shifting from annual crops to perennial grasses may lead to reduced water storage. However, the impact will vary depending on climatic zone (McIsaac et al. 2010). In contrast, perennial grasses may be used for managing water table in poorly drained soils (Mooney et al. 2009). But if poorly managed, fertilizer application, especially during establishment years may lead to water pollution due to leaching (Christian

Table 12.5 Biomass yield of selected bioenergy crops, potential ethanol production land area needed for different energy crops to meet 136 billion L of bioethanol required under renewable fuel standards

Feedstock	Harvestable biomass (Mg DM ha^{-1})	Ethanol production (L ha^{-1})	Land area needed	% of harvested US cropland
Corn grain	10.2	4266	31.0	22.9
Corn stover	7.4	2805	47.2	34.8
Total corn (grain + stover)	17.6	7071	18.7	13.8
Switchgrass	10.4	3936	33.7	24.9
	3.8	1438	92.1	67.9
Miscanthus	29.6	11,205	11.8	8.7

et al. 2006). Generally, proper management under perennial grasses reduces movement of pollutants compared to annual crops systems due to growth in early spring (Love et al. 2011; Ng et al. 2010; Love and Nejadhashemi 2011; Wu and Liu 2012) their extensive root system which enables lower nutrients requirements than annual crops. High yielding bioenergy crops such as miscanthus may be used to minimize the land demand for biofuel production. An example of the land requirement for selected bioenergy crops to produce 136 billion L required under Renewable Fuel Standard (RFS) by year 2022 in USA is presented in Table 12.5.

In addition to technological barrier which must be overcome to achieve sustainable second generation biofuels, the following must also be taken into consideration: (i) bioenergy crops may indirectly compete with food for arable lands, especially when large-scale feedstock are cultivated solely for the purpose of energy production, (ii) bioenergy crops require large water input, whereas renewable freshwater supply is a scarce commodity, and large population is at risk of recurring droughts. Climate change may also aggravate the drought risks by changing the hydrological cycle. This rises a moral dilemma of land and water for human need versus energy, (iii) lifecycle analysis for biofuels should take into account nitrogen (N), C and water footprint.

Lignocellulose biomass is comprised mostly of plant cell walls, which typically about 75% is polysaccharides, a valuable pool of potential sugars. Lignocellulose is made up of three major constituents, cellulose, hemicellulose and lignin (Fig. 12.6) and smaller part comprising extractives—pectin, protein, waxes, soluble non-structural materials such as sugars and nitrogenous compounds, and inorganic minerals (Jorgensen et al. 2007; Chandra et al. 2012). Cellulose, hemicellulose and pectin are carbohydrate polymers which typically comprise up to two thirds of the lignocellulose and are substrates targeted for generation of bioethanol. The proportions and molecular organization vary depending on the type of biomass. Typical ranges for selected plant species are presented in Table 12.6. The lignocellulosic biomass requires pretreatments to break its recalcitrance and release sugars contained within cellulose fibers. The prerequisite step for utilizing lignocellulosic biomass for producing liquid fuel is depolymerization of the plant cell

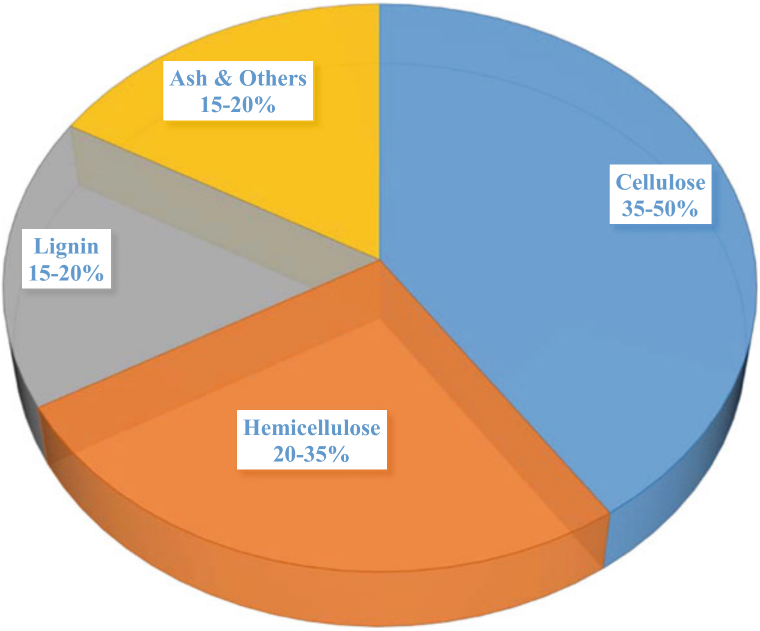

Fig. 12.6 General composition of lignocellulosic biomass

Table 12.6 Cellulose, hemicellulose and lignin contents of some lignocellulosic biomass materials

Plant biomass material	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Miscanthus	40	18	23
Switchgrass	45	31.5	12–20
Bermuda grass	25	35.7	9–18
Corn stover	32–40	17–35	7–18
Wheat straw	30	50	15
Rice straw	36–47	17–35	9–18
Softwood stems	45–50	25–35	25–35
Hardwood stems	40–55	24–40	18–25

wall polysaccharides to monomeric sugars. As a result, the potential of lignocellulose biomass feedstock has not been fully realized.

Lignocellulose is a cohesive composite material constructed around a framework of cellulose microfibrils, enduring the material with tensile strength and stiffness. In a cell wall, cellulose microfibrils are generally coated with hemicelluloses, a polysaccharide that bind to the outer surface of microfibrils, effectively producing a hairy coat which plasticize the material by maintaining the distance between the neighboring microfibrils and maintaining the flexibility in the material. The flexibility is particularly important during cell expansion. The microbial conversion of hemicellulose fraction, either in monomeric or in the oligomeric form is essential for increasing fuel yields from lignocellulosic material. It may also minimize C debt associated with land clearing, and even sequester C in the low C marginal lands. However, marginal lands may require substantial inputs and water resources to be able to produce economically sustainable biomass. Overall management practices such as crop choice, input intensity, harvesting strategy, will have major influence on the sustainability of cellulosic biofuels. One concern about introducing biomass crops in non-native environment is that some biofuel crops may be invasive and may impact local plant biodiversity.

12.7.2.2 Composition of Lignocellulosic Biomass

Cellulose

Cellulose $(C_6H_{10}O_5)_x$, is the most abundant biopolymer on earth. It is the main constituent of lignocellulosic biomass which forms plant cell wall, making up 15–20% of primary cell wall and as much as 50–60% of the secondary cell wall. It is a homogenous polysaccharide that consists of a linear chain of D-glucose units linked by β-(1,4)-glycosidic bonds to each other, and contains over 10,000 glucose units. The Cellulose strains are associated together to make cellulose fibrils. Microfibril is a structural unit thought to consist of an elementary fibril of about 36 β-(1,4-linked D-glucose chains bound together by hydrogen bonds that may be associated with additional non-cellulosic polysaccharides (Ding and Himmel 2006). Cellulose fibers are linked by a number of intra- and intermolecular hydrogen bonds (Li et al. 2010). The conformation of glucose residues in the crystalline cellulose core of cell wall microfibrils forces the hydroxyl groups into radical orientation and the aliphatic hydrogen atoms into axial positions. This leads to creation of strong inter-chain hydrogen bond between adjacent chains of cellulose sheet, which makes cellulose resistant to enzymatic hydrolysis. In addition, hydrophobic interactions between cellulose sheets protect cellulose from acid hydrolysis. Therefore, cellulose is insoluble in water and most organic solvents (Swatloski et al. 2002).

Hemicellulose

Hemicelluloses $(C_5H_8O_4)_m$, located in secondary cell walls, are complex heterogeneous branched biopolymers containing pentoses (β-D-xylose, α-L-arabinose), hexoses (β-D-mannose, β-D-glucose, α-D-galactose) and/or orgonic acids (α-D-glucuronic, α-D-4-O-methylgalacturonic and a-D-galacturonic acids) (Girio et al. 2010). They consist of about 100–200 sugar units. They are relatively easy to hydrolyze because of their amorphous, and branched structure (with short lateral chain) as well as their lower molecular weight (Li et al. 2010). Unlike cellulose, hemicellulose is not chemically homogenous, and different hydrolytic technologies and various biological and non-biological pre-treatment options are available for fractionation and solubilizing them. Hemicellulose sugars may be degraded to weak acids and furan derivatives which act as microbial inhibitors during fermentation step (Girio et al. 2010). In order to increase the digestibility of cellulose, large amounts of hemicelluloses must be removed as they cover cellulose fibrils limiting their availability for the enzymatic hydrolysis (Palmqvist and Hahn-Hagerdal 2000). Hemicelluloses are relatively sensitive to operation condition, therefore, parameters such as temperature and retention time must be controlled to avoid the formation of unwanted products such as furfurals and hydroxymethyl furfurals which later inhibit the fermentation process (Palmqvist and Hahn-Hagerdal 2000). While cellulose is a universal compound of plant cell walls, hemicellulose shows more variation among different classes of plants. One way to classify the orders of angiosperms in the plant kingdom is by distinguishing them based on the composition and structure of hemicellulose their hemicellulose (Dahlgren 1989). The composition of hemicellulose can also vary as a function of development stage of the plant.

Lignin

Lignin $[C_9H_{10}O_3(OCH_3)_{0.9-1.7}]_n$ is an aromatic polymer synthesized from phenylpropanoid precursors. It is a very complex heterogeneous mixture of biochemical compounds. The major chemical phenylpropane units of lignin consisting primarily of syringyl, guaiacyl and p-hydroxy phenol are linked together by a set of linkages to make a complicated matrix (Demirbas 2008). Lignin is a phenolic polymer that provides a hydrophobic surface to water conducting cells and provides structural rigidity needed for mechanical support. Lignin is very important for energy applications. Lignin is an energy-dense compound due to many C-to-C linkages that can be oxidized. Biomass with high lignin is desirable for combustion purposes. In contrast, lignin can negatively affect the yield of fermentable sugars obtained after enzymatic saccharification by shielding cellulose and by providing a surface that cellulosic enzymes adsorbs irreversibly. The composition of selected lignocellulosic biomass is presented in Table 12.2.

Due to higher amount of fermentable sugars, lignocellulosic biomass will yield more fuel per unit weight compared to 1st generation biofuels. However the recalcitrance of lignocellulose materials has delayed the production of alcohol from the biomass materials. Expensive pretreatments are necessary to break this recalcitrance. Reaching cost-effective cell wall saccharification (degradation of cell wall) into monosaccharides is the key which will lead to cellulosic ethanol to enter the commercial market. Understanding of both cell wall composition and architecture is critical for development of methods that can overcome the inherent recalcitrance of lignocellulosic biomass to decomposition and degradation both through pretreatment and the development of improved feedstocks through breeding and bioengineering (Himmel et al. 2007). Current pretreatments include physical methods such as milling and grinding, high pressure steaming, and steam explosion, and biological using lignin and/or cellulose degrading microorganisms, or chemical treatments such as alkali or acid treatment and use of solvents to solubilize parts of hemicellulose and lignin (Bessou et al. 2011).

12.7.2.3 Converting Lignocellulosic Biomass to Biofuels

Production of second generation biofuels relies on efficient processing of lignocellulosic biomass. There are four main routes for producing energy from biomass: direct combustion, thermo conversion—pyrolysis, gasification; biological conversion—anaerobic digestion, fermentation; and chemical conversion.

Direct Combustion

Direct combustion is the oldest and most commonly used method for converting biomass to heat, power, and combined heat and power in air. This method is applicable at all scales from domestic use of domestic stoves to industrial boilers and largest devices used for power generation. Different forms of biomass can be utilized for direct combustion, including fuel wood, wood chip, pellets, straw, and charcoal. However, the most efficient combustion is achieved when biomass boilers are used. Solid biomass pieces can also be mixed with coal in co-firing, which enables large power generating industry to reduce their C footprint by incorporation biomass as percentage of their feedstock.

Thermal Conversion

For the thermal conversion, high temperatures are used but energy is not produced directly from biomass. Biomass is converted to energy carriers such as synthetic gases, bio-oil, or methanol that have higher energy densities and lower transport cost with improved and more predictable characteristics (Wright et al. 2008). The two main thermochemical conversion are pyrolysis and gasification, which differ with respect of presence or absence of O_2/air.

In the pyrolysis, biomass is burned in a complete absence of O_2 at 400–800 °C (Laird et al. 2009; Babu 2008). The process is also known as fast pyrolysis (Woolf et al. 2014). Most of cellulose, hemicellulose and part of lignin is broken down into gases during pyrolysis (Wang et al. 2014). As the gases cool the vapors condense into bio-oil which has a potential as a substitute for fuel and as a feedstock for bioethanol and biodiesel production. The remaining biomass mostly comprising lignin form charcoal called biochar (Lehmann et al. 2006).

Gasification requires partial oxidation and temperatures of about 800 °C. At a low concentration of O_2 biomass is gasified into organic gases ("producer gas") and charcoal. The CO_2 and water vapor in the producer gas are chemically reduced to carbon monoxide (CO) and hydrogen (H_2). Producer gas contains 18–20% H_2, 18–20% CO, 8–10% CO_2 and 2–3% methane (CH^4) as well as trace amounts of higher hydrocarbons, water, N_2 (if air is used as oxidizing agent). Various contaminants such as small char particles, ash, tar, and oils may also be present. Partial oxidation in the gasification can be carried out using O_2, air, steam or a mixture of these. When air is used, a low heating value gas is produced that is suitable for use in boilers, engines, and turbines but not transporting in pipelines due to low energy density. Gasification with O_2 or steam produces medium heating value gas which is suitable for limited pipeline distribution as well as synthesis gas "syngas", typically 40% CO, 49% H_2, 3% CH_4, and 17% CO_2 on dry basis. Syngas can be used to make methanol, ammonia, and also can be converted to liquid fuels by Fisher-Tropsch synthesis process which was first developed by F. Fischer and H. Tropsch in 1923.

Biological Conversion

Two forms of biological conversions exist: anaerobic digestion, and fermentation. Anaerobic digestion is the breakdown of organic materials by bacteria in the absence of O_2. Almost every type of organic material can be processed, including paper waste, grass cuttings, food waste, industrial effluents, sewage and animal waste. Anaerobic digestion produces biogas, which contains about 60% CH_4 and 40% CO_2. Biogas can be burnt to generate heat as well as scrubbed and used to generate electricity. It can also be used as biofuel. The liquid and solid residue—digestate (byproduct) is used as soil conditioner. The amount of biogas and the quantity of digestates obtained vary according to feedstock used. More biogas will be produced if the feedstock is more liable to decompose. Sewage and manures produces less biogas because the animals that produced it has already removed some of energy content.

Fermentation is the biological process used for converting sugars into ethanol or other low molecular weight alcohols depending on microbial strain. Ethanol fermentation uses yeast (*Saccharomyces cerevisae*) and requires simple (monomeric) sugars as raw material. Yeast fermentation produces 0.51 kg of ethanol from 1 kg of C_6 sugars such as glucose and mannose or sucrose. Starch biopolymer requires a hydrolysis step first to break it down to simple sugars for fermentation. Polymer carbohydrates are also present in all plant cell walls, and can potentially provide the most abundant source of biofuel production. However, the carbohydrates (cellulose and hemicellulose) exist in the form of fibers and interlinked with lignin, requiring additional pretreatment and hydrolysis to release fermentable sugars.

Chemical Conversion

The main chemical conversion process is transesterification which is used for the production of biodiesel—fatty acid methyl esters (FAME). Lipids and oils either produced directly by crops or derived from vegetables and algae can be used to convert to biodiesel. Transesterification is used to transform the large branched molecular structure of oils into smaller, straight chained molecules similar to diesel. Three basic transesterification routes are: (i) base catalyzed transesterification, (ii) direct acid-catalyzed transesterification, and (iii) conversion of the oil to its fatty acids and then to biodiesel. The base-catalyzed the method is the most commonly used because it uses low temperatures (50–66 °C) and pressure (around 1.4 bar) with minimal reaction time, has high yield (98%) with minimal side reactions and no intermediate compounds.

12.7.2.4 Biorefinery Concept

Second biofuels are produced through biochemical and thermochemical processes. Similar to petroleum-based refineries, bio-based refineries are facilities that integrate conversion processes based on the use of biomass feedstock to produce transportation fuels, direct power, high-value chemicals and other useful commodities with minimal waste and emissions (Srirangan et al. 2012). Three major types of conversion are generally included in biorefinery with the aim of deoxygenize and depolymerize biomass feedstock to release monomeric sugar for subsequent conversion. These are (i) thermochemical and mechanical conversion, (ii) biochemical and biological conversion, and (iii) physicochemical conversion (Cherubini 2010). Biorefinaries are currently categorized into phase I, II, and III depending on the feedstock which can be processed and products produced. Phase III biorefineries are more complex and advanced in that they can handle multiple feedstock produce multiple products (Srirangan et al. 2012).

Biochemical process involves hydrolysis and fermentation or ‘wet process’ similar to 1st generation, except that the feedstock is generally vegetative biomass (lignocellulosic). Thermochemical process involves pyrolysis or gasification treatment. Two main approaches are used for biomass processing: (1) enzymatic processing—utilized for homogenous biomass, and (2) thermochemical processing—preferred for variety of feedstock including non-homogenous biomass and residues. The conversion of lignocellulose to ethanol involves three steps: pretreatment, hydrolysis and fermentation. The pretreatment separates lignin from cellulose and increases the porosity of the materials so that hydrolytic enzymes can access the substrates of cellulose and hemicellulose. Pretreatment can be either physical, chemical, or biological using microbes such as fungi to degrade lignin and break down hemicellulose (Cheng and Timilsina 2011). The lignocellulose is converted either biochemically or thermo-chemically.

In the biochemical process, cellulose and hemicelluloses are hydrolyzed and the hydrolysates are fermented to ethanol. The ideal approach of releasing soluble sugars from lignocellulose is to use cellulose enzymes (Cheng and Timilsina 2011). Enzymatic hydrolysis involves a series of biochemical reactions catalyzed by enzymes (Sharrock 1988). Soluble sugars can be fermented to ethanol by yeasts. In thermo-chemical process, the pyrolysis and gasification technologies are utilized to produce synthesis gas, from which a range of long C chain biofuels can be reformed (Sims et al. 2008). Other pathways which are several variations of these two are also under evaluation in research laboratories and pilot plants (Fig. 12.1, Sims et al. 2008; Chum et al. 2011).

Bioethanol can also be produced from cellulose and lignocellulose derived from the plant biomass. But the high pressure and temperature requirements of the conversion process incurs high energy costs (Ragauskas et al. 2006). However, there is scientific and technological initiatives to develop new technologies that will improve the efficiency of second generation biofuel production (DOE 2006; Ragauskas et al. 2006). The desired outcome of the new technological break-though is to develop biofuels that: (i) have greater energy efficiency than corn ethanol, (ii) have positive effects on nutrient cycling in crop ecosystems, and (iii) require minimal land conversion (DOE 2006; Field et al. 2007; Ragauskas et al. 2006; Fargione et al. 2008b; Gurgel et al. 2007). One way to achieve these outcomes will be to modify plant species through breeding and genetic engineering for sustainable biomass quantity and quality for biofuel production (Ragauskas et al. 2006).

12.7.3 Third Generation Biofuels

The third generation biofuels are derived from photosynthetic bacteria and algae which are either unicellular or multicellular autotrophic organisms which grows in aquatic environment and convert CO_2, water and sunlight through photosynthesis to produce lipids, carbohydrates, and proteins in large quantities (Ozkurt 2009). These organisms are recognized as excellent feedstock for 3rd generation biofuels due to their high oil/lipid and carbohydrate contents. There are several aspects of algal biofuel production that have combined to capture the interest of researchers and producers globally: (i) high biomass yields per unit area of cultivation producing greater amount of biomass, lipids and carbohydrates in short duration of time, (ii) cultivation strategies can minimize or avoid competition with arable land and nutrients used for conventional crop production. Algae can be produced via bioreactors with no requirement for arable land and other farming inputs such as fertilizers, and pesticides (Nigam and Sigh 2011; Carere et al. 2008), (iii) algae can utilize waste water, and saline water, thereby reducing competition for limited freshwater supply, (iv) algae recycles C from CO_2-rich flue emissions from stationary CO_2 sources—such as power plants and industrial emitters, (v) algal biomass is compatible with integrated biorefinery vision of producing a variety of fuels and valuable co-products (DOE 2016b), and (vi) require less energy than other feedstock during conversion to energy (Zhu and Ketola 2012).

Relative to other biomass, the aquatic biomass represent the strategy that can be executed on a large scale without any economic or environmental penalty (Aresta et al. 2005). Algae have unique adaptability to grow in adverse habitats both marine and freshwater environments. They are both unicellular and multicellular autotrophic aquatic plants. Algae do not have real roots, stems, leaves and embryos, and can be grown in shallow lagoons raceway ponds, closed ponds, photo-bioreactors, fermenters and sea-based systems. They are able to photosynthesize, but they do not contain typical plant organs.

Macroalgae are the most important component of marine ecosystems that serve as bio-resources for preserving and preventing eutrophication and pollution (Notoya 2010). Macroalgae are able to reach sizes of up to 60 m in length (McHugh 2003). Macroalgae belongs to lower plants in that they do not have roots, stems, and leaves. Instead, they are composed of thallus (i.e., leaf like structure) and sometimes stems and foot. Some species enclose gas-filled structures to help in buoyancy. Growth rate of macroalgae exceeds that of terrestrial plants. For example, uncultured brown algae biomass of average productivity is estimated at 3.3–11.3 kg dry weight m^{-1} yr^{-1} compared with 6.1–9.5 kg fresh weight m^{-2} yr^{-1} for sugar cane, a most productive land plant (Kraan 2010).

Macroalgae differ in various aspects such as morphology, longevity, and ecophysiology. They are classified based on their pigmentation into brown (Phaeophyta), red (Rhodophyta), and green (Chlorophyta) (Chan et al. 2006). About 200 species of macroalgae are used worldwide, and nearly 10 are intensively cultivated—including Phaeophyta—*Lumina japonica*, and *Undaria pinnatifida*; Rhodophyta—*Eucheuma*, *Gracilaria*, *Porphra*, and *Kappaphycus*; and Chlorophyta—*Enteromorpha* and *Monostroma* (Luning and Pang 2003). In Asian countries such as China, India, Philippines, South and North Korea, Indonesia, and Japan, macroalgae are cultivated for various uses such as food, feed, chemicals, cosmetics, and pharmaceutical products (Carlsson et al. 2007). There is a large potential for large scale culture in Atlantic waters (Kraan et al. 2000; Peteiro and Freire 2009).

Macroalgal biomass has a unique advantage for biofuel production—including: (i) their unique lifecycle enables them to be more productive, they can be harvested more than 5 times in a year, (ii) they can succeed and grow well in salty sea waters with only sunlight and available nutrients from the sea and no need of any chemical fertilizers, which saves energy, (iii) converting macroalgal biomass into biofuel offer some benefits of reducing impact on food security and minimizing C footprints on ecosystems, (iv) macroalgae have high carbohydrate content (Table 12.7)

Table 12.7 Carbohydrate content of macroalgae

Phylum	Species	Carbohydrates (%)	Potential biomass use
Chlorophyta (green algae)	*Ulva*	42.0	Methane, ethanol
	Enteromorpha	64.9	
	Monostroma	63.9	
Rhodophyta (red algae)	*Porphyra*	45.1	
	Rhodymenia	44.6	
	Gracilaria	61.8	Methane
Phaeophyta (brown algae)	*Laminaria*	39.9	Methane, hydrogen
	Alaria	39.8	
	Sargassum	33.0	Methane
	Padina	31.6	

Source Rajkumar et al. (2013), Dhargalkar and Pereira (2005) and low lignin compared to lignocellulose biomass which facilitates high mass production which can be converted to fermentable sugars, (Adams et al. 2009), (v) utilization of sea water and waste water bioreactors minimizes water crisis, (vi) with advancement of bioengineering, it is possible to develop suitable varieties of macroalgae which can be produced in bioreactors with the desirable biofuels characteristics (DOE 2016b).

Microalgae are photosynthetic microorganisms found in both marine and freshwater habitats. They are have been classified based on various characteristics such as pigmentation, photosynthetic storage products, the arrangement of photosynthetic membranes, and other morphological features. Currently microalgae are divided into four groups namely diatoms (Bacillariophyceae), green algae (Chlorophyceae), blue green algae (Cyanophyceae), and golden algae (Chrysophyceae) (Khan et al. 2009; Abomohra et al. 2016). The driving force behind the exploring of microalgae as an alternative energy source originates from its fast growing and highly efficient photosynthetic systems for C fixation and carbohydrate production and high lipid content (ranging from 20 to 40% dry weight; Table 12.8). During photosynthesis the algae are able to convert CO_2 and energy from sunlight into biomass and O_2. Algal strains are also capable of accruing oils through three types of production schemes: phototrophic (i.e., photosynthesis), heterotrophic (i.e., through dissimilation of carbonaceous substrates such as glucose), or mixotrophic (i.e., a mixture of phototrophic and heterotrophic) (Srirangan et al. 2012). The biomolecules such as carbohydrates, proteins, lipids, and nucleic acids are the common constituents in microalgae. Owing to their rapid growth rate, i.e., as high as 100 times faster than the terrestrial plants and can double their biomass in less than 1 day, microalgae have become attractive renewable energy source (Tredici 2010). Their simple cellular system and large surface to quantity

Table 12.8 The oil content of some microalgae species

Algae species	Oil content (% dry weight)	Bioethanol yield
Botryococccus braunii	25–75	
Clyindrotheca spp	16–37	
Chlorococcum humicola	19.2	0.52
Chlorococcum infusionum	19.2	0.26
Chlamidomonas reinhardtii	–	0.24
Isochrysis spp	25–33	
Monallanthus salina	>20	
Nannochloris spp	20–35	
Nannochloropsis spp	31–68	
Neochloris oleoabunans	35–54	
Nitzchia spp	45–47	
Phaeodactylum tricornutum	20–30	
Schizochytrium spp	50–77	

Source Chisti (2007), Rodolfi et al. (2008), Rajkumar et al. (2013)

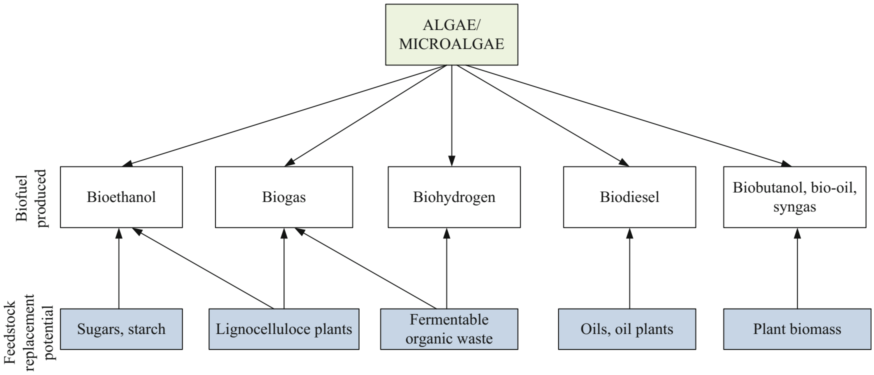

Fig. 12.7 Algal biomass feedstock and conceptual conversion routes for various bioenergy sources

ratio gives them the ability to utilize more amounts of nutrients from the source of water to support their growth rate (Khan et al. 2009).

Algae can produce several types of renewable biofuels (Fig. 12.7), including methane by anaerobic digestion of algal biomass (Spolaore et al. 2006), biodiesel derived from algal oil (Gavrilescu and Chisti 2005), and photo-biologically produced bio-hydrogen (Kapdan and Kargi 2006). The veg-oil algae can be harvested and converted to biodiesel, while algae carbohydrate content can be fermented to produce bio-alcohols. Some studies have shown that algae can produce as high as 60% of their biomass in the form of oil, which can be converted to biodiesel for use in transportation. Hence, the energy utilized for trans-esterification in the production of oil from alcohol and catalyst is eliminated. Algae can be grown on saline, arid, or drought affected land and has harvesting cycle of one to ten days. This minimizes the use of land for production of crops (Chisti 2007). Algae are also completely biodegradable and can be produced on ocean or freshwater. Although algal based oil production is technologically immature, few genetically modified algal strains can produce extremely high oil yield—up to 75% dry weight. It is estimated that microalgae can produce ~10 to 300 times more oil for biodiesel production than conventional dedicated energy crops in the near future (Nigam and Sigh 2011).

Biofuels production from algae has the potential role to play in the global energy sector and also minimizing environmental impacts associated with fossil fuel burning, while also providing other ancillary economic, social and environment benefits. Nevertheless, the research for biofuel production from algae is at the beginning if not an infant stage in light of realizing the potential benefits through commercially viable algal biofuel production. The main huddles to be solved involves the costs gap, since technologies available for large scale production of algae, harvesting, and processing (drying, energy conversion) are not economically viable. There is a substantial demand for research to improve and optimize both algae production potential and the economics of energy production in effort to achieve sustainable energy production from this renewable source with large theoretical potential. In addition to energy, developing biorefinery process which utilizes algae as the feedstock has the potential to support other chemical and pharmaceutical industries by producing co-products which can reduce the production and processing costs substantially.

12.8 Perspectives and Future Directions of Bioenergy

Replacement of fossil fuels will take place irrespective of current concerns, since the use of fossil fuels is causing significant harm to the environment. Several important bioenergy options such as sugar cane ethanol production in Brazil, waste-to-energy systems efficient traditional biomass for cooking and biomass based CHP are current by competitive and could provide synergies/overlap with longer term options. Lignocellulosic biofuels for replacing gasoline, diesel, and jet fuels and also advanced biofuels and bioelectricity generation and biorefinery concepts offers a competitive deployment in medium—2020–2030 and longer timeframe. Bioenergy hold the potential to provide more sustainable source of energy for both electric generation and transportation sector, if produced sensibly. The contribution of biofuels to solving the current and near future energy crisis relies on technological breakthrough to meet the projected short and medium term (2050) demand. Certain current systems and future and future options including perennial crops forest products and byproducts, biomass residues and advanced conversion technologies can offer significant GHG mitigation performances of as high as 90% reduction compared to fossil energy baseline. However, land conversion, forest management and land management that lead to loss of SOC pools and indirect land use change effects can reduce net positive GHG mitigation. To increase the potential for commercial bioenergy technology deployment and its success competition with food and fiber must be minimized, land must be properly managed, and agriculture and forest yields per unit land area must increase substantially.

Bioenergy has potential to mitigate GHG if resources are developed sustainably and efficient conversion technologies are applied. Despite its significant potential for climate change mitigation, deployment of large-scale bioenergy also carries considerable risks. Expansion of bioenergy without monitoring and good governance of land use carries risks of significant conflict with food supplies, water resources, biodiversity and low GHG benefits and even increasing GHG emissions. Implementation that follows effective sustainability framework could avoid such conflicts and enable realization of positive outcomes of rural development, amelioration of marginal and degraded lands and climate change mitigation. The climate change mitigation value of bioenergy systems depends on several factors, some of which are challenging to quantify. Sustainable technical potential of up to 100 EJ yr-1 to global primary energy supply by 2050 can be achieved. High GHG emission savings could be achieved if technological and governance preconditions are met, but such high deployment of land intensive bioenergy feedstocks could also lead to detrimental climate effects.

Performance of biomass production and use are site and region specific. As a part of good governance of land use and rural development, policies governing bioenergy expansion needs to take into consideration specific site and regional consideration and prioritize the land use and requirement. Priority should be given to agriculture (crops and livestock), forest and biodiversity requirements. Biomass resource potential interacts with climate change impacts, but specific impacts and regional differences regarding these interactions are still poorly understood. Replacing fossil fuels with biofuels reduces net CO_2 emissions, and with judicious selection of land for biomass production they can increase SOC sequestration. Perennial bioenergy cropping systems offer opportunities to combine adaptation measures—such as water retention, land degradation protection and modernization of agriculture with the biomass resources production.

Combining biomass energy with carbon capture and sequestration (CCS) increases the possibility of achieving envisioned GHG emission reduction and maintaining the global temperature increases to <2 °C. However, both biomass energy and CCS technologies are at the development stage and are not commercially available. Their implementation is heavily dependent on government subsidies. In addition, potential for advanced bioenergy, biomaterials, as well as the potential role of aquatic (algae) biomass is less understood and highly uncertain. The success of both biomass energy and CCS will require sustained investments that can enable technological breakthroughs and result in cost reduction, and implementation strategies that can gain public and political acceptance.

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Chapter 13
Carbon Capture and Storage in Geologic Formations

Abstract Carbon dioxide (CO_2) emissions, the most important anthropogenic greenhouse gas (GHG), can be reduced by CO_2 capture and storage (CCS). This strategy is applicable to many large stationary sources including power generation plants, oil and gas refinery, cement production and other industrial sectors generating large point source of CO_2. While the technology for CCS is currently available, significant improvements are needed to enhance confidence in storage security. In 1996, the first CCS project established for the purpose of mitigation of CO_2 emission began injecting CO_2 into deep geological formation in offshore aquifer in the North Sea, Norway. Since that time, science has advanced in areas such as geophysics, chemical engineering, monitoring and verification, and other areas, while also governments have funded demonstration projects at various sizes ranging from small-scale proof of concept to industrial-scale demonstration projects. Five industrial-scale CCS projects are currently operational globally with more than 0.035 Pg of CO_2 captured and stored since 1996. Observations from these industrial scale projects and commercial CO_2 enhanced oil recovery (CO_2-EOR), engineered natural analogues as well as theoretical consideration, models and laboratory studies have suggested that appropriately selected and well managed CCS sites are likely to retain almost all of injected CO_2 for long time and provide the benefits for the intended purpose of CCS. However, CCS is still struggling to gain foothold as one of the main options for mitigating climate change due to high costs, advances in other options including renewable energy, as well as discovery of shale natural gas and the associated hydrological fracturing extraction techniques, absence of international action by governments and private sectors on climate change, economic crisis-induced low carbon (C) prices, and public skepticism. The estimated costs for CCS varies widely depending on the application—such as gas clean-up versus electricity generation, type of fuel, capture technology, and assumptions about the baseline technology. Generally, for current technology, CCS would increase cost of generating electricity by 50–100%, and parasitic energy requirement of 15–30%. In this case, capital costs and energy requirements are the major cost drivers. In addition, significant scale-up compared to existing CCS activities will be needed to achieve intended large reductions of CO_2 emissions. For example, a 5- to 10-fold scale-up in the size of individual projects is needed to

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capture and store emissions from a typical coal-fired power plant of 500–1000 MW, while a thousand-fold scale-up in size of current CCS enterprise would be needed to reduce emissions by 1 Pg C yr^{-1}. The estimated global oil and gas reservoirs are 1000 Pg CO_2, saline aquifers global potential capacity ranges from 4000 to 23,000 Pg CO_2. However, there is considerable debate about how much storage capacity actually exists and is available for CCS, particularly in saline aquifers. Research, improved geological assessments and commercial scale demonstration projects will be needed to verify the estimated capacity and improve confidence in storage capacity estimates.

Keywords Carbon capture technologies · Coal-fired plants · Geological carbon sequestration · Saline aquifers · Enhanced oil recovery · Seismicity

Contents

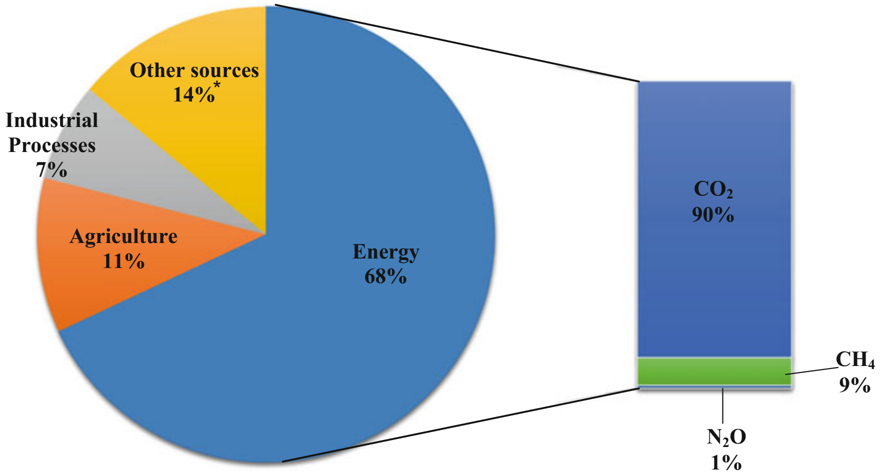
13.1 Introduction

A range of technologies which are collectively termed carbon dioxide (CO_2) capture and storage (CCS) are suggested as one of critical options in the portfolio of solutions available for combating climate change, allowing the emission reduction, and stabilization of CO_2 emissions, while also acting as a bridge to low C and C-neutral energy sources (IPCC 2005, 2014). CCS describes a process that separates a relatively pure stream of CO_2 from industrial or power plants and stores it in suitable geological formations after conditioning and compression (IPCC 2014). It is a process which involves the integration of four main steps: (i) the CO_2 capture, i.e., the separation of CO_2 from large point source such as large fossil fuel energy-related facilities and major CO_2 emitting industrial sources, (ii) compression of CO_2 from gas to liquid or denser gas to reduce the volume, (iii) transportation (i.e., transportation of pressurized CO_2 from point of capture and compression to the storage location, either by pipelines or other means), and (iv) storage (i.e., long-term storage of CO_2 by isolating it from the atmosphere), commonly by sequestering it in the geologic formations underground (IPCC 2005; Benson et al. 2012). Although it is applicable to other point sources, CCS research has mostly focused on capturing CO_2 from power generation fossil fuels—such as coal, or gas-fired power plants. In the short term, CCS could offer benefits of slowing growth of CO_2 emissions while other lower GHG emission energy technologies are maturing and deploy widely. Additionally, over the longer term, CCS could be used to reduce emissions from sources that are difficult to eliminate in any other way such as energy intensive industrial processes, natural gas clean-up, hydrogen production, fossil fuel refining, petrochemical industries, and cement production (Benson et al. 2012). The International Energy Agency (IEA) estimates that when fully implemented, CCS could contribute about 20% of CO_2 reduction by the end of this century (IEA 2008, 2013).

Technologies are currently available to carry out all four steps of CCS, but implementation of CCS remains a challenge because the cost of capturing CO_2 is too high for economical industrial scale deployment. Also, integration of CCS with electricity production or industrial processes has not been demonstrated at a large-scale, because of high costs of capturing CO_2 from the flue gas, and also, confidence needed that the storage of CO_2 in geological formation can be safe and effective over time periods of 1000 years and longer is still lacking. While in principle, CCS could be deployed on a much wider basis today, the challenges of deploying CCS, especially that of retrofitting pre-existing large point sources with CCS designed without the consideration of CCS as the future option should not be underestimated. Integration of CCS into existing power generation facilities and other industrial operations that demand highly reliable performance is destined to result into technological challenges, on top of large capital investments and significant operating costs required for CO_2 capture and storage. With todays' CO_2 capture technology, 10–30% of the energy output may be consumed by CO_2 capture unit alone depending on the age and type of power plant, and the degree of systems integration. The dated plants tend to be less efficient compared to the modern plants. Efficiency in both CO_2 capture technology and power generation will be needed to offset the energy penalty of CO_2 capture. An enormous effort has been devoted to advancing CCS technology, with 15 large-scale projects actively in operation globally, 7 more under construction, and 21 more in planning phase globally, although the final financial commitment decision remains pending for majority of them (GCCSI 2016). The CO_2 capture and storage capacity of these 22 projects in operation or under construction is estimated at 0.04 Pg CO_2 yr^{-1} (GCCSI 2016). In 2016, five industrial-scale demonstration projects, capturing 0.0005–0.002 Pg CO_2 yr^{-1} from different industrial sources and store it in deep geological formation, have been operational for several years around the world, demonstrating that, at least on a limited scale and size, CCS can be safe and contribute to reducing CO_2 emissions. Four of these capture CO_2 from natural gas clean-up, while in the fifth, CO_2 is captured from coal-to-synthetic natural gas plant. None of the operating industrial-scale projects takes CO_2 from coal-fired power plants, however, and only two of the current projects under construction will capture CO_2 from power plant.

The captured CO_2 is generally purified and compressed before being transported to the storage sites. The majority of the ongoing research and demonstration efforts have been devoted to CO_2 removal from stationary large CO_2 emission sources which include power production sources, mostly because: (i) these sources are by far the dominant contributors of total anthropogenic CO_2 emissions accounting for nearly 60% of GHG emissions (Victor et al. 2014), (ii) the technologies of capturing CO_2 from the stationary sources is more mature than those for capturing CO_2 from mobile sources such as transportation devices, (iii) based on economies of scale—it is more attractive to implement CCS technologies on large-scale power plants for some foreseeable future (IPCC 2005). Fossil fuel power plants are the most susceptible to CO_2 reduction mandates, due to large point source. Therefore, CCS may be strategic for their future CO_2 mitigation options. Furthermore, unlike other energy intensive industries, power plants cannot move to other countries with fewer CO_2 emission restrictions.

Fossil fuel derived energy presently dominates most aspects of modern human activities and the modern day way of life. Fossil fuels are also projected to remain as the main source of energy for the foreseeable future. Although United Nations Framework Convention on Climate Change (UNFCCC) and Kyoto Protocol cover a wide array of CO_2 sources and other greenhouse gases (GHGs) responsible for climate change, the combustion of fossil fuels in both stationary and mobile sources remains the largest source of GHG emissions, including CO_2 which accounts for 35% of total anthropogenic GHG emissions in 2010 (Bruckner et al. 2014). Fossil fuels are currently supplying more than 80% of total primary energy demand. Among the many anthropogenic GHG sources, the energy is by far the largest source releasing 68% of anthropogenic GHGs in 2010, of which, about 90% of energy-related emission is CO_2 originating mostly from fossil fuel combustion while CH_4 and N_2O account for 9 and 1%, respectively (Fig. 13.1; IEA 2015a). Energy sector CH_4 emissions originate from oil and gas extraction, transmission, and distribution, and N_2O from energy transformation, industry, transport and buildings (IEA 2015a). Other sectoral emissions include agriculture (11%), industrial processes (7%) and other sources (14%) (IEA 2016; IPCC 2013). The share of energy-related CO_2 emissions from coal increased from 38 to 44% between 2000 and 2014, while that of natural gas remained at 20%, and that of oil declined from 42% in 2000 to 35% in 2014 (IEA 2015a).



*Other sources include: biomass burning, peat decay, indirect N_2O emissions from non-agricultural emissions of NO_x and NH_3, waste and solvent use.

Fig. 13.1 Shares of global anthropogenic greenhouse gases emission in 2010. *Data source* IEA (2016)

Suitable techniques for capturing CO_2 were originally developed circa 1950 for use in food processing, chemical manufacturing and in connection with the production and utilization of natural gas as the energy source as well as H_2 purification (Zaman and Lee 2013). The technology involved scrubbing the gas stream with chemical solvent, producing pure CO_2 as a valuable product for use in food processing and chemical manufacturing. The capture process itself was a relatively small scale compared to those needed for power plants (Zaman and Lee 2013). Subsequently these techniques were adapted for capturing CO_2 from flue gas streams of coal or natural gas combustion systems for carbonation of drinks and CO_2-enhanced oil recovery (CO_2-EOR). In these processes, CO_2 is obtained as a valuable product also, and the capture process is relatively small as compared to those needed for power plants to mitigate CO_2 emissions. Therefore, when existing CO_2 separation techniques are implemented on large-scale power plants they are not cost-effective (DOE/NETL 2010) due to much higher volumetric rate of low pressure flue gas that is needed to be processed and the presence of other impurities such as SO_2. As a result, when CCS is implemented in a typical pulverized coal power plant the cost of electricity is estimated to increase by up to 80% and the generating capacity decrease by as high as 30% (Zaman and Lee 2013). Horn and Steinberg (1982) are among the first to suggest the process used to separate CO_2 from natural gas and utilization of separated CO_2 for EOR as a method to control CO_2 emission.

Even though the industry has been pushing for the adoption of CCS as the significant breakthrough mitigation option since its inception, the Intergovernmental Panel on Climate Change (IPCC) was hesitant to recognize it as one of an appropriate CO_2 mitigation pathway earlier, and it was not listed among the recognized mitigation options in the IPCC Second Assessment Report published in 1995 (IPCC 1995), and in its Third Assessment Report of 2001, CCS also received much less attention (IPCC 2001), probably due to relatively lack of in-depth risk analysis. In 2002, the 7th Conference of Parties to the UNFCCC invited the IPCC to conduct a scientific assessment of potential for CCS as a CO_2 emission mitigation option, which resulted into publication of a special report on CCS in 2005. Publication of the Special Report on CCS by the IPCC in 2005 (IPCC 2005) and the support by influential bodies such as the International Energy Agency (IEA) (IEA 2004, 2009) gave CCS the much needed credibility. However, the climate change summit of Copenhagen Denmark in 2009 appears to be the turning point in the perception of CCS, due to its lack of global signal that climate change mitigation must be taken seriously in investment decision, with industries finding less emphasis in climate change mitigation and lack of reasons to invest in deployment of CCS on a large-scale since it adds significantly to the cost of power generation and other products that involve the use of fossil fuels.

There has been a wide divergence of opinion about the feasibility, long-term risks, and even the very need for CCS. Whereas, CCS has been offered as a vision of future in which the impacts of growing fossil fuel reliance are minimized by capturing and storing CO_2 instead of allowing it to accumulate in the atmosphere (Jaccard 2005; IPCC 2005), and some have projected that CCS is a technology critical to solve the climate change while continuing the reliance on fossil fuels, and conclude that CCS is an essential tool for reducing CO_2 emission to the atmosphere sufficiently quick to avoid worse consequences of climate change (IPCC 2005; IEA 2008, 2013; Gibbins and Chalmers 2008b), others believe it will not make significant contribution to solving the climate change problems, and still others believe CCS to distract from making needed decisions to begin phasing out fossil fuels immediately in favor of renewable energy sources and C-free or C-negative energy sources. Some researchers have argued that investing in CCS is not money well spent, as the global climate-energy situation are becoming increasingly dire, bold measures with the near-term influence are needed to reduce, rather than sustain fossil fuel reliance (Stephenson 2013). It has been suggested that the vision of CCS has enabled complacency about the growing dangers of fossil fuel dependence by providing a false sense of optimism, and therefore, investments in CCS need to be halted (Stephenson 2013).

Regardless of ongoing debate in scientific community, knowing whether CCS is part of climate change solution or not will likely take many decades, and the answer will most likely be heterogeneous, with some regions and industries adopting it as part of the preferred sets of options for reducing emissions and others finding other mitigation alternatives. Only when the decision makers widely recognize that slow and incremental change will not solve the climate change problem will it be clear that every possible option is needed to address GHGs emission and climate change. The objectives of this chapter are to present the global narrative of CCS in terms of some current technological and scientific understanding and developments.

13.2 What Is Carbon Dioxide Capture and Storage?

The CO_2 capture and storage involves capturing CO_2 arising from large point sources such as combustion of fossil fuels in power generation, preparation of fossil fuels—including natural gas processing, biomass based fuels, certain industrial processes such as production of H_2, ammonia, iron and steel, cement, and ethanol fermentation (Benson et al. 2012). Capturing of CO_2 involves separating the CO_2 from other gases in flue gas stream—including N_2 and water vapor. The captured and purified CO_2 is compressed into liquid or high density gas and then transported to the storage site where it can be stored and separated from the atmosphere for long time or permanently for the explicit purposes of avoiding atmospheric GHG emissions. The potential sequestration sites include depleted natural gas and oil reservoirs, underground sedimentary basins and saline aquifers, and coal seams that cannot be mined. A number of studies have explored technological and scientific dimensions of CCS. The greatest focus of ongoing research and demonstration of CCS has been on techniques for capturing CO_2 from coal-based electric power generation, logically so, because nearly 40% of total anthropogenic fossil fuels CO_2 emission is from the application of coal as a feedstock for power generation. Coal-fired power plants also dominate the lists as the biggest stationary CO_2 point sources. In addition, the global resources of coal are significantly large compared to other fossil fuels (Fig. 4.3). A typical coal power plant emits 0.8–1.0 Mg CO_2 per Terawatts hour (TWh = 10^{12} W h) of net electricity generated, and a 1000 MW electrical coal power plant at a 75% annual load factor emits about 6000 gigagrams (Gg = 10^{12} g) CO_2 yr^{-1} (Benson et al. 2012). Much of the ongoing research has focused on scientific understanding of CO_2 capture, transport, and storage processes, but relatively less attention has been given to regulatory, legal, long-term permanence, public perceptions, economic, and future liability considerations, even though these elements are as important for any successful implementation of industrial-scale CCS projects.

The goal of CCS is to reduce emissions from large stationary sources such as power generation, natural gas processing, hydrogen (H_2) production from coal or gas, cement manufacturing or steel making. A full lifecycle emission using CCS technology on individual facility can reduce 65–85% of CO_2 emission from fossil fuel (Benson et al. 2012). Some of the remaining emissions involves activities beyond the plant boundary. Assessments under a range of stabilization scenarios suggest that the contribution of CCS is anticipated to be 20% of needed reduction over the next century—which is similar to that of renewable energy and use efficiency gains (IPCC 2005; IEA 2008). In the future, CCS may also contribute to emission reduction from transportation sector through H_2 production and use for light and heavy duty vehicles, electrification of vehicles, and production of synthetic fuel using captured CO_2.

Although the major focus of capturing CO_2 for climate change mitigation has been coal-fired power generation plants, there are several important industrial applications that produce nearly pure CO_2 vents. These include raw natural gas and synthesis gas (syngas) purification, production of high value products (e.g., ammonia, other synthesis gas products such as H_2, synthetic natural gas (SNG) from coal, coal-to-liquids, ethanol fermentation, or methanol production). These have been the major focus of the ongoing small scale technology demonstration projects due to relatively higher CO_2 concentration and lower costs of purification. Most of H_2 is made from natural gas via CH_4 reforming process which does not produce pure CO_2 stream however, (Shah et al. 2007), but H_2 made from heavy oil, petcoke or coal gasification produces large pure CO_2 stream. Other industrial point sources of CO_2 include cement kilns, iron/steel manufacturing, oil refinery and bulk chemicals. The large industrial point CO_2 sources have typically released less than 10^6 Mg CO_2 yr^{-1} which are relatively small sources compared to large power generation plants. Nevertheless, the higher purity of industrial CO_2 vents makes them targets for CCS due to lower costs of CO_2 capture and purification. Countries such as China with many large-scale coal gasification plants and large synthesis gas capacity for ammonia, methanol, and H_2 have large pure CO_2 vents for lower cost CCS (Simbeck and Roekpooritat 2009). Key determinants of the extent of CCS deployment include: (i) capacity for storage in appropriate sites in geological formations, (ii) policy framework to encourage emission reduction, (iii) lack of low-cost opportunities for reducing emissions such as renewable energy or nuclear power, (iv) pace of technological progress to lower the cost of geological storage, (v) interest in deployment of CO_2-EOR at large-scale, (vi) public acceptance, and (viii) access to large-scale capital investment needed for CCS projects.

13.3 Energy Consumption and Carbon Dioxide Emissions

Fossil fuels are the predominant primary energy present in the world and accounted for nearly 87% of commercial energy use carriers in 2014 (BP 2015). Fossil fuels are also the dominant fuel for power generation, producing about two thirds of electricity currently, and projected to provide a similar fraction in 2035 (IEA 2015c). However, they also account for most of local conventional pollution and global CO_2 emissions. Due to advantages in cost, technological maturity, and established infrastructure, fossil fuels are likely going to remain as a major component of global energy supply for a foreseeable future. However, relying on fossil fuels has posed major challenges to the world which need to be addressed, including: (i) climate change, (ii) air pollution, (iii) lack of affordable efficient alternative energy carriers, and (iv) energy insecurity.

Electricity demand has been increasing with economic growth. Due to high CO_2 emission from power generation sources, majority of current GHG mitigation research effort are devoted to CO_2 removal from the stationary power production sources. In addition, these sources share many similarities with the existing processes where CO_2 capture has been used for several decades, and therefore, technologies for CO_2 capturing from stationary sources are more mature than those from the mobile sources such as transport devices. Economies of scale also make it economically attractive to implement CCS technologies on large power plants, at least within some foreseeable future. The CO_2 emissions from fossil fuel energy sources represent about 60% of the global anthropogenic GHG emissions. In 2013, fossil fuels accounted for 82% of the global total primary energy supply (TPES) (IEA 2016) and contributing 70% of CO_2 emissions (IEA 2014). Oil, coal, and natural gas represented 31, 29 and 21% of the global TPES, respectively in 2013, but coal accounted for 46% of the global CO_2 emissions due to its heavy C content per unit of energy released, while oil and natural gas contributed 33 and 20%, respectively (IEA 2016). In 2013, 163.6 Exajoules (EJ) (28.9%) of coal, 179.9 EJ (31.7%) of oil, and 121.5 EJ (21.4%) of natural gas were consumed by the world economies (IEA 2015b; IPCC 2011). Since the industrial revolution, annual CO_2 emissions from fossil fuel combustion dramatically increased from near zero in 1750 to 10.1 Pg C in 2014 (Fig. 13.2; Le Quéré et al. 2015, 2016). Growing global energy demands from fossil fuels play a key role in observed increasing trend in fossil fuel CO_2 emissions. Average decadal CO_2 emission growth since 2000 is estimated at 2.5% yr^{-1} (Le Quéré et al. 2015, 2016).

The global TPES increased by nearly 150% between 1971 and 2013 (Fig. 13.2), mainly relying on fossil fuel, and fossil fuel use continues to grow worldwide, especially in countries with rapidly developing economies. The growing world

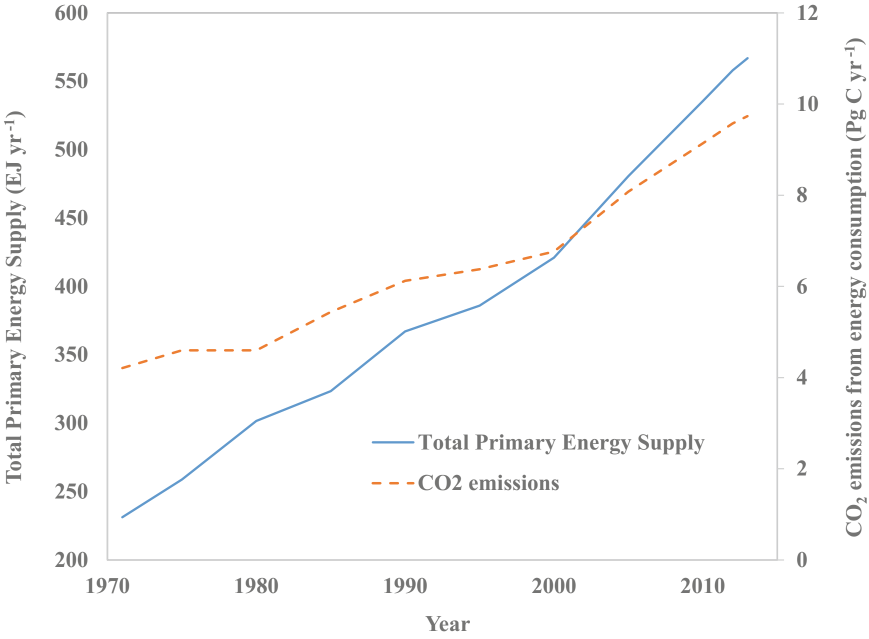


Fig. 13.2 Primary energy supply changes and CO_2 emissions from fossil fuel use from 1971 to 2013. *Data source* IEA (2016), Le Quéré et al. (2015, 2016)

energy demand from fossil fuels plays a key role in increasing trends of CO_2 emissions. The global primary energy consumption grew at an average rate of 1.4% yr^{-1} between 1990 and 1995; 1.6% yr^{-1} between 1995 and 2001, 2.6% yr^{-1} between 2001 and 2015, and more than doubled from 231.44 EJ in 1971 to 567.0 EJ in 2013 (Fig. 13.2; IEA 2015b, 2016). The contribution of global CO_2 total emissions from industrialized economies decreased from 66.5% in 1971 to 38.3% in 2013, but this decline is mostly attributed to increased emissions from developing economies, dominantly China and India rather than decline in emissions from industrialized economies (IEA 2016). In 2013, power and heat generation was by far the largest CO_2 emission sources, accounting for 42% while the transport sector accounted for 23% of CO_2 emissions (Fig. 13.3), implying that targeting CO_2 emissions from stationary energy generation sector by CCS could have greater impact in climate change mitigation.

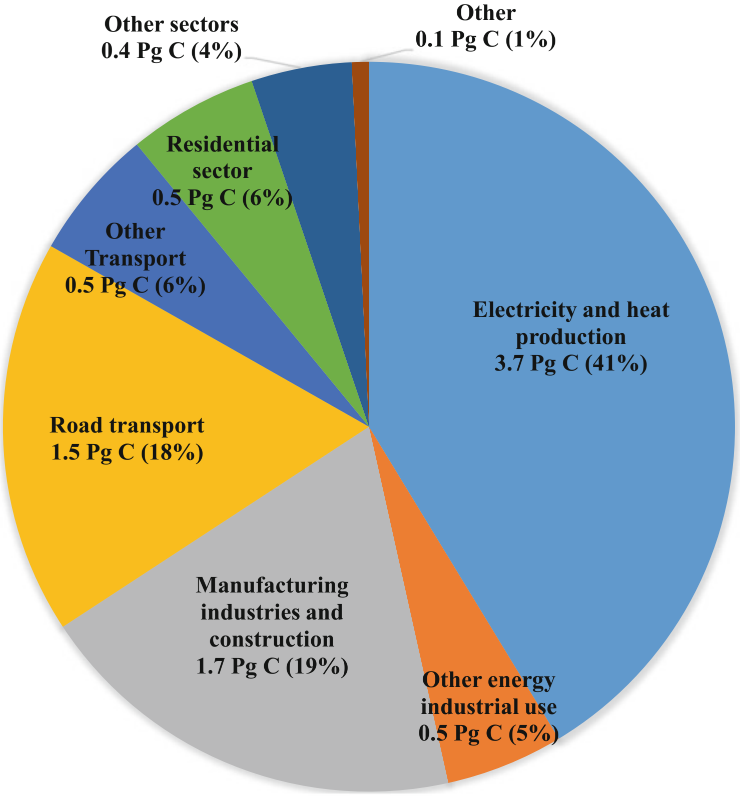


Fig. 13.3 The global CO_2 emissions by sector in 2013. *Data source* IEA (2016)

13.4 History of Carbon Capture and Storage

The injection of CO_2 underground was not totally new technology when it was first suggested for climate change mitigation. The suggestion of capturing CO_2 derived from anthropogenic large point sources and disposing it in the ocean as a way to control the atmospheric CO_2 increase and climate change mitigation was first proposed in 1970s by Marchetti (1977) who suggested that the Mediterranean undercurrent entering the Atlantic at Gibraltar had sufficient capacity to store all of CO_2 produced in Europe until the year 2100 and beyond. In addition, Horn and Steinberg (1982) were among the first to suggest a process for separating CO_2 from the natural gas purification and use it in EOR as a way of controlling atmospheric emissions of CO_2. In the 1970s and 1980s, as the production from oil fields in the USA was declining, oil companies started injecting water, natural gas, and CO_2 to recover more oil and extend the production lifetime of oil reservoirs. However, the CO_2-EOR was done almost exclusively using CO_2 from natural underground CO_2 reservoirs, so it was not leading to climate change mitigation. Nevertheless, CO_2-EOR provided the practical experience and understanding of the behavior of CO_2 underground, the knowledge of suitable cap rock that can sustain CO_2 best, and also the best injection pressures for CO_2, as well as wells placement and pipeline transportation of CO_2 (Dooley et al. 2010). In 1990s and 2000s, climate change mitigation emerged to become a global policy agenda, and resulting to UNFCCC by 1992, and the Kyoto Protocol in 1997 which included commitments of all developed countries to reduce their GHGs emission. However, not all developed countries ratified or complied with the Kyoto Protocol provisions. Despite Kyoto commitments and other subsequent international agreements on climate change mitigation, addressing the seemingly unstoppable CO_2 emissions from fossil fuel combustion remained an urgently challenging problem without a viable solution agreeable to major stakeholders. Today, CO_2-EOR remains a main driver of CCS, and many demonstration projects have used CO_2 for EOR as a way to minimize the costs for CCS projects.

In 1996, Startoil began injecting 0.001 Pg CO_2 yr^{-1} into an aquifer 800 m beneath the North Sea at Sleipner, Norway (Torp and Gale 2004). The CO_2 for the injection was stripped from Sleipner natural gas to meet the specifications for sale of natural gas in Europe. Startoil was faced with CO_2 emission tax of \$50.00 ton^{-1} of CO_2 emitted, but opted to inject CO_2 into a seabed aquifer to avoid paying CO_2 emission tax, and this process began an entirely new approach for controlling CO_2 emission. By the end of the century and beginning of 21st century, the legal and regulatory framework, as well as risks associated with underground CO_2 and societal acceptability was gaining attention within scientific community, as well as national and international agencies. Two other industrial-scale CCS demonstration projects—one in Canada (Weyburn) and one in Algeria (In Salah Gas Project) were established (Riddiford et al. 2003; White et al. 2004; Fig. 13.4). The success of these initial projects led to the optimism that CCS can apparently be a promising option to contribute significantly to climate change mitigation within a short period

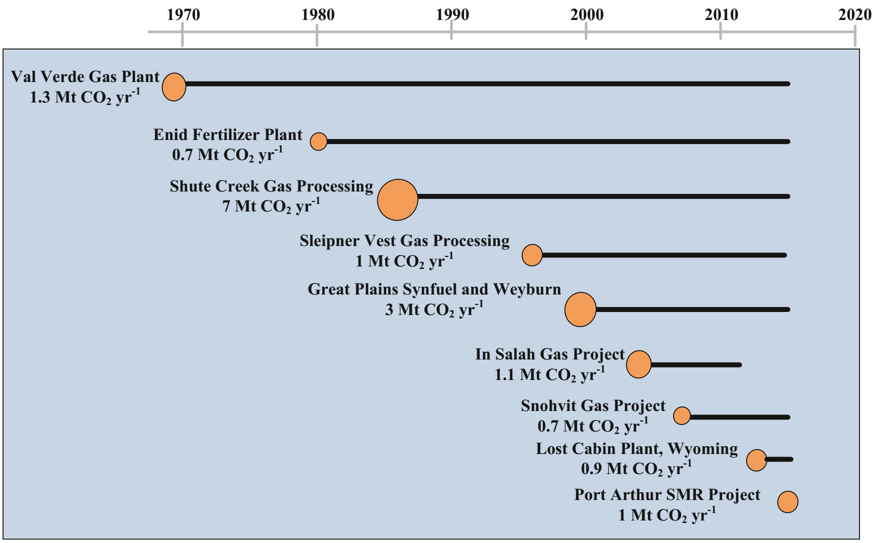


Fig. 13.4 Timeline of starting dates of operational CCS industrial-scale demonstration projects. *Circle* size distinguishes approximate annual mass of CO_2 stored, while *black lines* represents operation timeline

of time since the late 2000s. However, the pace of deployment of new projects has slowed, even though governments and private sector investment in science and technology of CCS has continued to build a strong and broad foundation for it.

The option of storing CO_2 in ocean has largely been abandoned since the publication of the IPCC Special Report on CCS (IPCC 2005), primarily due to: (i) high costs, (ii) low storage permanence, and (iii) significant ecological and environmental impacts. The current discussions and research have revolved around the injection of CO_2 into geologic reservoirs and other storage options including CO_2 mineralization, but techniques involving CO_2 mineralization are expected to play a limited role in climate change mitigation (Wang et al. 2014; Boot-Handford et al. 2014). Some of the full scale operational industrial CCS demonstration projects that store atmospheric CO_2 are presented in Fig. 13.4. Six industrial-scale projects have been operational globally and exclusively for the purpose of demonstrating CO_2 emission mitigation from the inception of CCS in 1996 to present, injecting 0.0007–0.003 Pg CO_2 yr^{-1}, mostly for EOR. Five of the successful commercial-scale CCS projects that have been injecting approximately 0.001 Pg CO_2 yr^{-1} are:

1. Startoil's Sleipner offshore gas platform in the North Sea, Norway, injecting CO_2 from natural gas purification into undersea deep saline formation.
2. Weyburn, Saskatchewan, Canada injecting CO_2 from Dakota Gasification (brown coal (lignite) gasification via synthetic natural gas (SNG) purification) plant from North Dakota, USA. Purified CO_2 is piped to Weyburn and used in CO_2-EOR.

3. Wyoming, USA facility injecting CO_2 from natural gas purification, which is piped to Power River Basin of Wyoming and used for CO_2-EOR.
4. BP's In Salah facility in Algeria, Africa with CO_2 from natural gas purification with injection to the same formation but at a distance from the production well. The injection operation has been terminated.
5. Startoil's Snøhvit Project in Norway, which injects CO_2 from liquefied natural gas facility into a saline formation underneath the Barents Sea.

All the successful commercial-scale demonstration projects have the economic advantage of producing large pure CO_2 vent from raw natural gas purification or other sources. Natural gas from the fields contains about 2% to more than 15% CO_2, and CO_2 removal is required to meet natural gas pipeline energy content specifications regardless of the CO_2 mitigation policy. The early 1970s through early 1990s, projects did not use CCS for the climate change mitigation, nevertheless, they provided considerable CO_2 emission reduction, as well as understanding the injection conditions. The first project implemented solemnly for climate change mitigation purposes was Sleipner project, which is located at offshore Norway. The In Salah gas project in Algeria has ceased to operate. Recovery of hydrocarbon in oil from CO_2-EOR provides economic basis for the CCS project sustainability. The incentive behind Statoil's Sleipner and Snøhvit projects is the European CO_2 emission tax for operations in Norway. Therefore, the overall costs of these CCS projects have been significantly lower than normal CCS costs due to an added economic value of CO_2 capture and/or utilization.

There has been considerable debate whether CO_2 used for EOR should be considered as CO_2 storage for the climate change mitigation purposes? While amount of CO_2 remaining underground varies from site to site, and from oil well to oil well, it is estimated that about 50% of the injected CO_2 never returns to the surface (Stevens et al. 2003). Moreover, in almost all cases, the CO_2 produced with the oil is separated and injected back into the oil reservoir, primarily because CO_2 in this case is a valuable commodity, and avoids the need to purchase more CO_2. It can also be argued that the CO_2 emitted into the atmosphere when oil is used negates the benefits of storage, however. In the US, where most of CO_2-EOR is carried out, CO_2 utilization credits for EOR projects are \$0.53 per 1000 standard cubic feet (28.3 m^3) in EOR terms, which is significantly less than the total cost of CCS, unless the CO_2 is being captured regardless of CO_2 mitigation issues.

About 40 projects of different CO_2 injection scale ranging from 0.0006 to 0.004 Pg CO_2 yr^{-1} are in various stages of development globally (GCCSI 2016). Nevertheless, experience over the past suggests that only few of these are likely to be fully implemented (GCCSI 2016). The proposed projects under development indicate that CO_2-EOR continues to play an important role in demonstrating CCS at industrial scale (GCCSI 2016). Although CCS was designed to capture CO_2 from power plants and large industrial sources, none of the projects currently under operation takes CO_2 from power plant, and only one of the projects under development will utilize CO_2 captured from the power plant (GCCSI 2016). Although there has been large investments by governments and private sector in science and technology of CCS, similar progress has not been made in social, legal dimensions, and significantly lower private sector financial commitments to CCS have occurred. The economic crisis of 2008 and the related low price of CO_2 emission allowance units in the European Trading Scheme as well as sudden availability of significant quantities of shale natural gas at low prices in the United States of America have resulted in drop in funding for CCS projects in both USA and Europe. Moreover, the worldwide drop in costs of wind and solar energy production is making it a viable option for many households also, while reducing the enthusiasm of CCS.

13.5 Technology for Capturing and Transporting Carbon Dioxide

Coal-fired power plants have been the primary focus for CCS research, mainly due to the magnitude of emissions. Of all stationary CO_2 sources, electricity production is the largest single category accounting for more than two-thirds of global CO_2 emissions from stationary sources. Nearly 40% of human-made fossil fuel CO_2 emissions are from electric power generation (Benson et al. 2012). Although there are other applications, and feedstocks for CCS, coal-fired power plants also dominate the list of biggest stationary CO_2 point sources. However, all existing industrial CCS applications currently in operation are for industrial applications such as natural gas clean-up, biofuel production, and production of synthetic natural gas from coal, mainly due to high costs for capturing CO_2 from power generation. Only one of the commercial scale demonstration project currently captures CO_2 from coal-fired power plant. However, CCS can also be applied to other stationary CO_2 emission sources, including industrial sources such as steel mills, cement plants, ethanol production facilities, and natural gas processing units that remove impurities such as CO_2 and H_2S.

13.5.1 Carbon Dioxide Capture

The CCS requires large CO_2 stationary point sources within reasonable distances of suitable geologic storage locations. It is recommended that the suitable geologic formation should: (i) be deeper than 800 m, (ii) have a thick and extensive cap seal, (iii) have sufficient porosity for large volumes of CO_2 storage, and (iv) sufficiently permeable to permit injection at high rates without requiring overly high pressure (Benson and Cole 2008). Injecting CO_2 below 800 m provides two advantages: (i) CO_2 density is high enough to allow pore filling and decrease buoyancy difference compared with the insitu pore fluids, (ii) to protect underground water sources. The effectiveness of geologic CO_2 sequestration depends on how much CO_2 can be injected into subsurface rock formations, how long it will stay trapped there, and whether the process of subsurface injection and storage will have negative environmental consequences. All these factors are both technical and socioeconomic constraints that must be evaluated realistically before the CCS project implementation.

For the CCS technology to contribute in reducing CO_2 emission, CO_2 must come from the existing sources through retrofit or replacing the existing power generation plants with new plants with CCS. For a new plant constructed with CCS without replacing the old plant, the captured CO_2 is considered as CO_2 emissions avoided, which will slow the rate of growth of CO_2 emissions with no impact on reducing the existing CO_2 emission levels. Reduction of CO_2 emission requires retrofitting the existing fleet of coal-fired power plants with CCS, or replacing the existing fleet with lower CO_2 emission sources and/or retrofitted with CCS to significantly lower CO_2 emissions from current sources. Also, adding CCS to old existing plants are subject to net capacity and efficiency losses (Simbeck and Roekpooritat 2009). The CCS can also be applied to other types of stationary CO_2 sources including industrial sources such as boilers and blast furnaces, steel mills, cement plants, ethanol production, ammonia production plants, natural gas processing units that remove impurities such as CO_2 and H_2S, and electricity production from both coal and natural gas (IPCC 2005; Benson et al. 2012; IEA 2013) although research on CO_2 capture from these sources has received less attention. CCS in power plants tends to be among the most challenging in terms of financial perspective due to economy-wide increasing costs for power generation. However, electricity production is the largest single source accounting for more than two-thirds of global CO_2 emission from stationary sources. The sources of stationary CO_2 emissions are distributed around the world, but two countries that stands out in coal-fired power generation emissions are China and the United States of America (Yang and Cui 2012).

Technologies for geological storage of CO_2 build on long experience of oil and gas industry in pumping and managing subsurface fluids, including injection of CO_2 to increase oil production (EOR). Capture involves separation of CO_2 from industrial flue gas stream and its concentration. CCS requires concentration of CO_2 to purities of 95% or greater (IPCC 2005). High CO_2 concentration sources minimize purification and compression costs and also makes effective and efficient use of available sequestration resources—i.e., subsurface pore volume. The majority of cost for CCS lies in the CO_2 capture and purification stage. Current rates of geologic CO_2 sequestration are still small (on the order of few million metric tons of CO_2 per year (NETL 2015). To play a significant impact on climate change mitigation, much higher rates of CO_2 injection are needed as envisioned in IPCC Special Report on CCS (IPCC 2005), which has so far not yet been achieved in the ongoing research and demonstration projects. The capture and transport of CO_2 pose some of the principal challenges in the implementation of geologic C sequestration. For example, power plants that utilize CCS technologies are expected to require 10–40% more energy than equivalent plants without CCS. Depending on where in the combustion process the separation of CO_2 occurs, there are three technological pathways for capturing CO_2 from power generation: (i) pre-combustion capture, (ii) post-combustion capture, (iii) oxyfuel combustion (Fig. 13.5; Benson et al. 2012). The comparative advantages and drawbacks of these steps are summarized in Table 13.1. In the post-combustion CO_2 capture, a separation of CO_2 is added after the boiler without inherently changing the power generation system. Most of the demonstration projects in the power sector aim at post-combustion CO_2 capture. The first step of CO_2 recovery or capture and concentration to high purity CO_2 stream is the most expensive and it can normally be implemented through one of the three above named general processes (IPCC 2005).

13.5.1.1 Pre-combustion Carbon Dioxide Capture

Pre-combustion CO_2 capture involves conversion of fuel feedstock (i.e., coal or biomass or a mixture of coal and biomass) into syngas through gasification, steam reformation, or partial oxidation, and then shifting the syngas chemically to H_2 and CO_2 at elevated pressures, typically 30–70 atmospheres, and then separating H_2 from CO_2. The CO_2 can then be separated to leave H_2-rich fuel gas. Pre-combustion capture allows C to be stripped before the resulting H_2 gas is combusted. This process for power generation requires an integrated gasification combined cycle (IGCC) plant, of which only few are currently operational globally, and retrofitting for this type of plants is therefore, practically impossible. The separation of CO_2

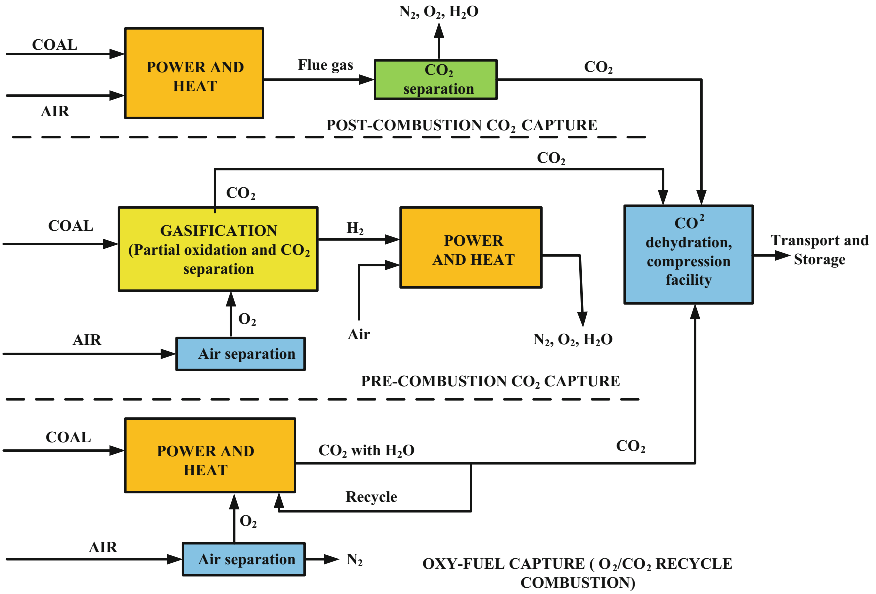


Fig. 13.5 Principles of three main carbon dioxide capture options (after Gibbins and Chalmers 2008a)

Table 13.1 Comparative advantages and disadvantages of post-combustion, pre-combustion and oxy-combustion

Technology	Advantages	Disadvantages
Post-combustion	• Mature technology for other application (e.g., separation of CO_2 from natural gas) • Standard retrofit of generation capability • Technology improvements and cost reductions possible with additional development	• High energy penalty (approximately 30%) • High cost
Pre-combustion	• Lower costs than post-combustion capture • Lower energy penalties than post-combustion capture • High pressure of CO_2 reduces compression costs • Combines with H_2 production for transportation sector • Technology improvements and cost reductions are possible with additional development	• Complex chemical process is required for gasification • Repowering of existing capacity is needed • Large capital investment is needed for repowering
Oxy-combustion	• Avoids the need for complex post-combustion separation • Potentially higher generation efficiencies • Technology improvements and cost reductions is possible with additional development	• New high temperature materials are needed for optimal performance • On-site oxygen separation unit is needed • Repowering of existing capacity is needed

typically uses physical solvent at the higher pressure, and then CO_2 is released as the pressure is reduced to regenerate the solvent. In the pre-combustion capture, CO_2 is not available for capture prior to combustion, but all fossil fuels can be gasified (i.e., partially combusted or reformed) with sub-stoichiometric O_2 and some steam at elevated pressures [typically 30–70 atmospheres (3–7.1 MPa)] to produce synthesis gas mixture of predominantly CO and H_2. Additional steam is then added and the mixture is passed through a series of catalyst beds for the steam-gas shift reaction to approach equilibrium (Eq. 13.1)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{13.1}$$

The CO_2 can be separated to leave a H_2-rich fuel gas. The separation process typically uses a physical solvent, where CO_2 is dissolved at higher pressure and then released as the pressure is reduced (Gibbins and Chalmers 2008a). No heat is required to regenerate the solvent, since CO_2 can be released at above-atmospheric pressure. Therefore, the energy requirement for CO_2 capture and compression in pre-combustion systems may be of the order of half that required for post-combustion capture. However, pre-combustion capture systems have to pay an efficiency penalty for the CO shift reaction (Eq. 13.1), and even without CO_2 capture, there is lost mass of CO_2 that does not pass through the turbines and generate power. Additionally, the efficiency of H_2 burning gas turbines is lower than conventional natural gas or syngas units, since heat transfer coefficients are higher for combustion products from H_2-rich fuels (Gibbins and Chalmers 2008a).

Pre-combustion Carbon Dioxide Capture in Electric Generation

Pre-combustion CO_2 capture in electric generation is mostly focused on coal through IGCC, and not natural gas combined cycle (NGCC). The NGCC-CO_2 capture is more focused on post-combustion CCS because no major modifications for standard NGCC design is necessary (Benson et al. 2012). In coal-fired power plants, when coal reacts with O_2 and steam at high temperatures and pressure, it produces syngas—a mixture of carbon monoxide (CO) and hydrogen (H_2) in a process of gasification. After gasification step, syngas reacts with steam in a water-shift reactor, which converts CO to CO_2, producing a mixture of CO_2 and H_2. CO_2 is then captured from this fuel gas, leaving just H_2 for the power generation. Generally, CO_2 is isolated along with minor amounts of CO, water, and O_2. This type of power plant is called IGCC power plant using coal, biomass, or their mixture. The sulfur compounds are removed from fuel gas prior to the CO_2 capture. When pre-combustion capture is applied to natural gas power plants, natural gas is first converted to syngas in the presence of O_2 and steam through reforming process. The fuel conversion steps are costly in pre-combustion CO_2 capture (Folger 2013).

Industrial Pre-combustion Carbon Dioxide Capture

The pre-combustion CO_2 capture has the most commercial experience. Most of the existing large-scale CCS projects have been from industrial applications involving CO_2 capture from pre-combustion capture from industrial oil and gas application and not electric power generation. There are natural gas purification and gasification-based synthesis gas (H_2 + CO) purification plants that remove CO_2 at amounts greater than 1 Pg CO_2 yr^{-1}, however, that high purity CO_2 is normally vented. The CO_2 is removed just to meet product gas—generally natural gas or H_2 specifications. Examples of industrial gasification plants with pure CO_2 vents with CCS include Dakota Gasification SNG plant in USA, the Shell Oil Pernis refinery in the Netherlands, and Shenhua Group liquefaction plant in China. Gasification is commonly used for production of H_2, ammonia, synthesis gas for chemicals, and natural gas in industrial settings. Pre-combustion CO_2 capture in electric generation is generally focused on coal through IGCC and not NGCC. The biggest challenge facing pre-combustion CCS currently is the high capital costs.

13.5.2 Post-combustion Carbon Dioxide Capture

Post-combustion CO_2 capture involves capture of CO_2 from flue gas after the power generation step, and the separation of CO_2 is mainly from N_2 and relatively little amounts of O_2 and water vapor. Post-combustion CO_2 capture is mainly for pulverized coal, oil-fired or gas-fired power plants, but it can also be applied to IGCC, NGCC and gas capture. Post-combustion separation requires the use of liquid solvents to remove the CO_2 from the flue gas, followed by extraction of the CO_2 from the solvents. The advantages of post-combustion capture include: (i) all existing power plants can be retrofitted with only minor modifications, (ii) energy demand of power plant can be controlled by adjusting the CO_2 capture level or by bypassing the CO_2 capture step at times of peak loads, and (iii) it can be applied to capture CO_2 from industrial manufacturing (e.g., cement production, steel industry (IPCC 2005). Post-combustion capture in electric generation has gained greater interest than industrial sources in recent years due to: (i) decreased interest in pre-combustion CO_2 capture as a result of high capital costs and slow commercial acceptance of IGCC with or without CCS, (ii) improved designs for post-combustion CO_2 capture with more vendor competition and choices of chemical solvents, (iii) minimal impact on traditional NGCC power plant process other than the large need of low pressure steam for CO_2 stripping and CO_2 compressor power, (iv) ability to easily bypass the back-end flue-gas scrubber process when problem with the CO_2 system occur or when there is a need for additional peaking power, and (v) lower capital outlay and ease retrofit to the existing power plant, however, moderately high capacity and efficiency losses and additional space are needed (Benson et al. 2012). Most interest in natural gas based electric generation CCS is with post-combustion CO_2 capture for CO_2 emission avoidance reasons. Lower natural gas prices and improved supplies are making NGCC more competitive with coal-based electric generation for baseload power.

Due to low concentrations of CO_2 (4–15% by volume) and low overall stream pressure in comparison to traditional sources of CO_2 where the feed gas is at high pressure, the partial pressure of CO_2 in flue gas is much lower. In industrial post-combustion, the CO_2 concentration in flue gas varies widely, from 7 to 10% for gas-fired boilers to 14–33% for cement kilns (IPCC 2005). Since CO_2 at such a low concentration cannot be captured effectively by physical adsorption, chemical absorption is likely needed, because physical adsorption depends on partial pressure for adsorption, whereas chemical absorption is less dependent on partial pressure. Reasons for inefficiencies in post-combustion CO_2 capture include the low concentration of CO_2 in the flue gas, large volume of flue gas to be treated, the requirement to compress CO_2 from the atmospheric pressure to storage pressure, and the relatively high temperature of flue gas which needs to be cooled before CO_2 capture. Temperature and pressure swing adsorption and membranes can also be used for separating CO_2 from N_2 in post-combustion capture. However, flue gas contaminants such as SO_2 cause problem to remove and negatively impact the performance of many technologies such as adsorption. In addition, the gas is almost saturated with water, making selective absorption or adsorption of CO_2 relative to water critical.

13.5.2.1 Physical and Chemical Processes for CO_2 Separation

Several technological options are available for separating CO_2 from a gas stream, and the optimal choice depends on the CO_2 source, the cost, and the ease of deployment. These include: (i) separation of CO_2 using sorbents or chemical solvents, (ii) membrane separation, and (iii) distillation of liquefied gas stream. The choice of technology particularly depends on CO_2 composition of the flue gas. For natural gas turbines the CO_2 concentration ranges from 3 to 4% for natural gas turbines, 10–15% for pulverized coal-fired plants and up to 40–60% for IGCC plants (IPCC 2005). Absorption into physical and chemical solvents, adsorption onto solid substrates, cryogenic separation, transport through CO_2 selective membranes, and mineralization are some of the options used for CO_2 separation (Wilcox 2012; Zaman and Lee 2013). Adsorption process is basically composed of two steps, adsorption and regeneration which operates on a repeated cycle. For CO_2 capture using solvents and sorbents, two-step process is required in which CO_2 is first removed from gas stream using absorption tower, and in second, CO_2 is released from the media in a separate regeneration tower. The low concentration of CO_2 in the flue gas of fossil fuel power plants necessitates large absorption towers for CO_2 separation and the related high costs of CO_2 capture. For natural gas cleanup, cryogenic separation and membrane separation are used, although on a limited basis. Amine solvents (Rochelle 2009), chilled ammonia (Mathias et al. 2010), ionic liquids (Goodrich et al. 2010), polymer membranes (Du et al. 2011) and cryogenic separation are some of potential options for CO_2 capture (Table 13.2). Monoethanolamine solvents are the most mature option and remain the benchmark for cost and technical performance evaluation (Rochelle 2009). Fundamental research in the area of CO_2 separation has grown rapidly and advances have been made across the board (Boot-Handford et al. 2014). The energy required for CO_2 capture is one of the biggest challenges for CCS. From thermodynamic perspective, the minimum energy required depends on CO_2 concentration, and ranges from 3 to 6 kJ mol^{-1} of CO_2 for coal fired plants and 7–9 kJ mol^{-1} of CO_2 for a natural gas plant, which represent only 2–3% of the energy output at the power plant (Wilcox 2012), suggesting that if efficient separation process could be developed, the energy penalty is small. However, in practice, the total energy penalty is significantly greater, about 5–10 times the minimum energy requirement (House et al. 2011). Reducing the energy penalty for CO_2 capture is one of the largest possibilities for lowering the CCS costs.

Table 13.2 Physical and chemical separation approaches for CO_2 capture

Method	Description	Example materials	Advantages	Technological challenges	References
Absorption	CO_2 from gas stream dissolves in fluid and subsequently released from fluid by changing pressure or temperature	Aqueous amine solutions, chilled ammonia, ionic liquids	Established technology with numerous solvent options. Rapid improvements in energy requirements achieved	Reducing energy for regeneration. Solvent degradation	Boot-Handford et al. (2014), Mathias et al. (2010), Rochelle (2009)
Adsorption	CO_2 from the gas stream adsorbs onto solid and subsequently released by changing pressure or temperature	Zeolites, metal organic frameworks, activated C	Potentially lower energy requirement for regeneration	Adsorption capacity and kinetics	Hasan et al. (2013), Banerjee et al. (2008)
Cryogenic	CO_2 is cooled until it becomes solid that separates from the gas stream	None	Avoids the need for solvents or sorbents. Lower energy requirements	Solid separation and handling	Tuinier et al. (2010)
Membranes	CO_2 from pressurized gas stream is preferentially transported through membrane	Polymer membranes, inorganic membranes	Avoids regeneration and energy requirements	Permeability selectivity	Yang et al. (2008), Du et al. (2011)
Mineralization	CO_2 reacts with calcium or magnesium-bearing rocks to form magnesite or calcite	Magnesium silicates, alkali rich waste streams	CO_2 is converted to a solid substance that can be reused as a building material or disposed of surface facilities	Rate of reactions, Mass reactants such as sources of Ca, Mg	Goff and Lackner (1998), IPCC (2005)

13.5.3 Oxy-Fuel Combustion Carbon Dioxide Capture

The third approach for CO_2 capturing is the O_2 combustion, where fuel is combusted under pure O_2 stream or a mixture of CO_2 and O_2 (IPCC 2005). Oxy-fuel combustion CO_2 capture is generally a post-combustion capture, but since the fuel is burnt in pure O_2 instead of air, the exhaust gas contains CO_2 and water. Therefore, CO_2 can be separated by condensation of the water. Coal gasification and oxy-combustion both produce gases that are more enriched in CO_2, thus simplifying or avoiding the need for liquid solvent extraction, but requiring more extensive investment in pre-combustion equipment (Thambimuthu et al. 2005; Rubin 2008). The advantage of oxy-fuel combustion is the lower cost of post-combustion capture. O_2 is generally separated from air (Fig. 13.5). In addition to CO_2 and water vapor, the post-combustion waste may also contain mixtures of trace gases, including O_2 and CO, thus avoiding the need to separate CO_2 from N_2 after combustion. The separation of O_2 from the air is a mature technology, albeit energy-intensive process using cryogenic separation. However, the air separation to generate pure O_2 required for combustion can be large for large scale power plants. Almost three times more O_2 is required for oxy-combustion power plant compared to IGCC power plant of equal size (Folger 2013). Oxy-fuel combustion CO_2 capture is also the least developed technology among the three CO_2 capture processes. However it continues to gain interest and development, likely due to its potential advantage of greatly simplifying the overall CO_2 capture process and avoiding most of the chemical processing associated with pre-combustion and post-combustion CO_2 capture. Oxy fuel combustion also has the potential to increase existing process efficiency in retrofit applications (Benson et al. 2012). The viability and appropriate choice of CO_2 capture depends on the specific power plant. A schematic flow of CO_2 sources, capture techniques, purification and geological storage is presented in Fig. 13.6.

13.5.4 Carbon Dioxide Capture from the Air

Some researchers have been promoting the idea of capturing CO_2 directly from the ambient air using various chemical absorption approaches (APS 2011). This approach will be able to capture non-point CO_2 sources such as mobile transportation fuels from mostly oil. Practical and economically competitive CO_2 capture is a major challenge due to low ambient air pressure and low CO_2 concentration at about 400 ppm. The ultra-low CO_2 partial pressure of just 0.0004 bar (40 Pa) atmospheric pressure likely will require strong bases to capture most of CO_2 from the air as well as very large adsorber or absorber. This could also mean large energy requirements to regenerate the CO_2 from strong basic sorbent into high purity CO_2 stream for compression.

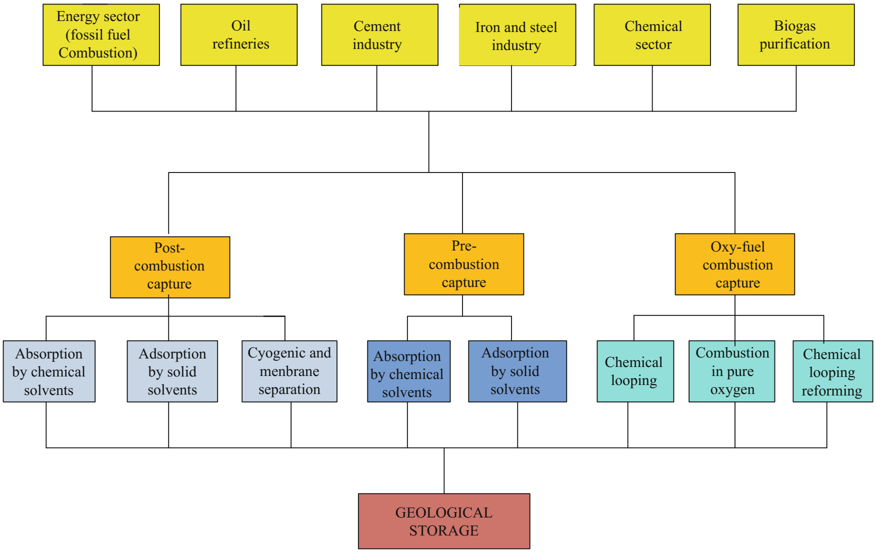


Fig. 13.6 Schematic diagram illustrating different possible sources of carbon dioxide, different capture, separation approaches and storage

13.6 Carbon Dioxide Transport

As outlined previously, CCS is a more distinctly technological approach that begins with the capture and compression of CO_2 from large point sources, followed by purification to obtain nearly pure CO_2. Purified CO_2 is then compressed to liquid for transport and injection. The chemical and physical properties of compressed CO_2 play an important role in the feasibility of geologic CO_2 sequestration. CO_2 becomes a liquid when compressed to high pressures for transport. When CO_2 is subjected to the combination of higher pressures and temperatures that characterize geological CO_2 injection sites, it becomes what is known as a supercritical fluid. The CO_2 is generally transported in three states: gas, liquid, and solid through the land or by the sea. The commercial transport uses tanks, ships and pipelines for gaseous and liquid CO_2. Gas transported at a close to atmospheric pressure occupies large volume and large facilities are also needed for its storage. Therefore, compression allows volume reduction, and it can further be reduced by liquefaction, solidification, or hydration. Liquefaction is an established technology for gas transport by ship—such as liquid petroleum gas (LPG) and liquid natural gas (LNG) which can be transferred to CO_2 transport. Experience of transporting CO_2 by truck or ship is mainly found in the food and brewery industry where CO_2 is generally transported as a compressed liquid (e.g., −50 °C, 0.7–0.8 MPa). Transportation of CO_2 by ship or train requires infrastructure development, including loading and unloading and temporary CO_2 storage, which makes the option more costly. Transport through ships, trucks, and train is not regarded as preferred option for large-scale systems (IPCC 2005). Pipeline transport is currently the most matured transportation option. In pipeline transportation, the volume is reduced by transporting CO_2 at high pressure which is routinely done in gas pipelines operating at pressures between 10 and 80 MPa. The large-scale storage projects will generally require pipelines transport, and for pipeline transport, CO_2 is compressed to a liquid or dense phase at the ambient temperature (i.e., CO_2 pressure above ~8 MPa), with temperature varying with location, but generally lower than 20 °C (Benson et al. 2012). At this temperature and pressure, CO_2 would have a density between 800 and 1200 kg m^{-3}, where larger mass per unit volume can be transported. There are more than 5800 km of CO_2 pipelines in operation in the United States transporting liquid or dense phase CO_2 with pressures above 7.38 MPa and sectioned typically less than 30 km (Parfomak et al. 2009). The CO_2 pipelines are generally made out of carbon-steel, for transporting relatively clean CO_2 without internal coating. Studies have demonstrated that CO_2 transport by pipeline does not pose higher risk of accidental leak than that tolerated for transporting other hydrocarbons by pipelines (Liu et al. 2015; Han et al. 2015; Koornneef et al. 2010). However, transporting CO_2 by pipeline through densely populated area will require modifications to current standards for increased safety, including increased pipeline wall thickness, and protection from damage (e.g., through burying the pipeline) (Koornneef et al. 2010).

13.6.1 Transportation Operational Issues

13.6.1.1 Pressure Drop

Frictional loss of pressure occurs as the CO_2 flows through the pipeline, which is dependent on pipeline diameter, CO_2 flow velocity, viscosity and density, and pipe roughness factor. At constant temperature, pressure drop in a 50.8 cm pipeline transporting CO_2 in dense phase is about 30 kPa km^{-1} (Gale et al. 2009). Pressure drop is generally overcome by increasing the inlet pressure to the pipeline so as to maintain at least 7.38 MPa, or installation of pressure boosters every 100–200 km for longer pipelines (Benson et al. 2012).

13.6.1.2 Corrosion

Components such as SO_2, NO, and H_2S form acid compounds in the presence of water, and it is highly corrosive. In addition, H_2S could react with C steel and form film of iron sulfide (FeS) which may dislodge at times and cause operational problems in the CO_2 compression units. Control of water content by dehydration is therefore essential for safe, cost-effective pipeline operation. Other options include use of protective coating and corrosion inhibitors, but these increases pipeline cost.

13.6.1.3 Hydrate Formation

CO_2 may form hydrate compounds in the presence of water and H_2S, which can block or plug the pipeline and also damage equipment. Hydrate formation can largely be stopped by drying the CO_2 and removing free water. The maximum allowable water content is in the range of 50–500 ppm (Benson et al. 2012).

13.6.1.4 Other Factors

Other important factors for CO_2 transport include operating temperatures and impurities. Operating temperatures are generally dictated by the temperature of the surrounding soil or water, and can range from below zero to as high as 20 °C in the tropics. CO_2 cools dramatically during decompression, as a result, pressure and temperature must be controlled during routine maintenance. Also, depending on the source of the flue gas, and type of CO_2 capture process, CO_2 streams may contain trace concentrations of H_2S, SO_2, NO, O_2, HF, Hg, N_2, and Ar which may impact the physical state of CO_2 stream, CO_2 compressibility, CO_2 density, pipeline integrity, safe exposure limits, and the minimum miscibility pressure of the CO_2 in oil, and impact the use of CO_2 in EOR among other factors (Benson et al. 2012).

13.6.2 Cost of Carbon Dioxide Capture and Transportation

The estimated cost of CO_2 capture in power plants and industrial production processes vary greatly and generally have high uncertainty. Global CCS Institute indicates that CCS would add approximately 40% to the cost of power production in IGCC and natural gas combined cycle plants, and between 50 and 80% for coal-fired power plants with post-combustion or oxy fuel combustion (Irlam 2015). For steel production, CO_2 capture will add 10–15%, while for cement production CO_2 capture will add 39–52% costs. Overall, costs for CO_2 capture will remain highly uncertain until industrial-scale projects are fully implemented. The CO_2 transport costs are a function of pipeline length, diameter, material, route of pipeline, and the safety requirements among other things. Overall, the transport of CO_2 by pipeline benefits from economies of scale, i.e., average transport costs decrease as scale increases. Therefore, larger diameter pipelines are preferred.

13.7 Carbon Dioxide Storage

Storage of CO_2 in deep geological formations has been under development since circa 2000, and is now considered as one of the feasible components in the portfolio of options for reducing GHG emissions. Other options for CO_2 storage which have been assessed include ex-situ mineralization, ocean storage in dissolved or liquid forms, and CO_2 reuse in the chemical industry. Among the options of storage, only storage in the geological formation is considered to have the capacity, permanence and environmental performance necessary for storage at large scale needed to reduce CO_2 emissions (IPCC 2005; Benson et al. 2012). The geological formations suitable for CO_2 storage occur in sediment basins, and include depleted or depleting oil and gas reservoirs and salt water (saline) filled rocks. The ongoing large-scale industrial scale demonstration projects together with CO_2-EOR, mostly in North America, have provided valuable experience base for assessing the potential for geological storage of CO_2 and efficacy of C storage. The projects have also demonstrated that, for CCS to contribute to the scale needed for large reduction of CO_2 emissions required, a 250-fold increase per year is needed compared to amount currently being sequestered, and effectively sequestering such large volumes requires building a strong scientific foundation for predicting the coupled hydrological-geochemical-geomechanical processes that govern the long-term fate of CO_2 in the deep sub-surface geological strata. Also, additional methods for characterizing and selecting suitable storage sites, subsurface engineering to optimize performance and cost, safe operations, monitoring technologies, remediation methods in case there is a leak, as well as regulatory oversite are required. In addition, the international institutional approaches for managing long-term liability risk are also needed.

Beginning in the early 1990s, there was a great deal of interest in storing CO_2 in the ocean, and two approaches were pursued: (i) biological sequestration through ocean fertilization, and (ii) direct injection of concentrated stream of CO_2 in the ocean. In 2001, the Southern Ocean Iron Experiment was conducted in the Southern Pacific (Buesseler et al. 2004; Coale et al. 2004). Results from this and similar experiments demonstrated rapid increases in biological productivity. However, many questions regarding long-term ecosystem impacts and the effectiveness of this technique in lowering atmospheric CO_2 concentration remain unanswered (Breitbarth et al. 2010). Also, the permanence of stored CO_2 remains debatable. As a result, ocean fertilization is not under serious consideration for large-scale CO_2 storage.

Injection into the mid-depth ocean (1000–3000 m deep) where CO_2 can stay for thousands of years before returning to atmosphere through ocean circulation, or near-bottom of the ocean to create stationary pools of CO_2 have also been proposed. Concerns about biological impacts, high costs, lack of permanence of ocean storage, and also concerns about public acceptance have decreased interest and investment in ocean storage. Although under sufficiently cold ocean at water depths greater than 3000 m, CO_2 transitions from being lighter than water to heavier than water, and remains on the ocean bottom (Schrag 2009), over time the CO_2 will dissolve into ocean water leading to ocean acidification and gradual release back to the atmosphere. It has been proposed to inject the CO_2 under thin layer of ocean bottom sediments therefore, combining some aspects of geological and ocean storage (Schrag 2009). This technique is not well developed, and is a subject of research. Another ocean storage which has been proposed combines CO_2 with sea production of methane hydrates, such that as CH_4 is released from hydrate structure, CO_2 could replace it (Ohgaki et al. 1996). Of these options, currently only the storage in geological formation is considered to have capacity, permanence, and environmental performance necessary for CO_2 storage at scale needed to materially reduce CO_2 emissions and potentially mitigate climate change (IPCC 2005; Benson et al. 2012).

13.7.1 Storage of Carbon Dioxide in Deep Geological Formations

The Earth's crust is made up primarily of three types of rocks: (i) igneous rocks—formed by cooling magma from either volcanic eruptions or magmatic intrusions far beneath the land surface, (ii) sedimentary rocks—formed as thick accumulations of sand, clay, salts, and carbonates over millions of years, and (iii) metamorphic rocks—these can be of either origin that have undergone deep burial with accompanying pressure and thermal alteration. The sedimentary rocks located in the so called sedimentary basins have been the primary focus for ongoing geological storage of CO_2 because the geological storage on geological timescales has already been proven through the presence of oil and gas accumulation in these formations. Sedimentary basins underlie much of the continents, and some of them are co-located with major CO_2 emission sources. In the past few years, there has also been a significant effort to understand the potential of volcanic rocks—primarily basalt, which rely on geochemical reactions between CO_2 and basalt for storage of CO_2 (McGrail et al. 2006). Motivation for evaluating storage in basaltic rocks are: (i) some countries with large CO_2 emissions—such as India, Brazil, and USA are underlain by basaltic rocks, (ii) to test the hypothesis that large fraction of stored CO_2 would be converted to stable minerals such as calcite or magnesite and a assure permanent storage of CO_2 (Aradottir et al. 2011; Oelkers and Cole 2008).

Sedimentary basins often cover thousands of meters of sediments with tiny pore spaces (e.g., 10^{-3}–10^{2} μm diameter) in the rocks which are filled with salt water (saline aquifers) and where oil and gas reservoirs are generally found. Sedimentary basins also consist of many layers of sand, silt, clay, carbonates, and evaporate rock formations—composed of salt deposited from evaporating water. The sand layers provide storage of oil, water, and natural gas. The silt, clay, and evaporate layers provide the seal that can trap these fluids underground for millions of years and longer. Geological storage of CO_2 in the sedimentary basins below silt and clay layers aim at taking advantage of the seal much the same way that oil and natural gas are trapped (Gunter et al. 2004). Possible storage formations in sedimentary basins include oil reservoirs, natural gas reservoirs, saline aquifers, and also unmineable coal beds. The overlying thick continuous layer of shale, silt, clay, or evaporate is the single most important feature of geologic formation that is suitable for geological storage of CO_2 which prevent upward migration of CO_2 by combination of viscous and capillary forces. The presence of oil and natural gas reservoirs is a good demonstration of presence of suitable reservoir seal. For the saline aquifer formations, a significant site characterization effort is required to demonstrate the presence of a satisfactory primary seal. The important attributes of the seal include low permeability (in the order of 10^{-18} m^2 or less) and high capillarity entry pressure (1 MPa or more) (de Coninck and Benson 2014). In addition to CO_2 storage below the seal, CO_2 may also be retained through secondary trapping mechanisms such as solubility (Gilfillan et al. 2009), residual trapping and mineral trapping (Michael et al. 2010; Krevor et al. 2012). In saline aquifers, where pore spaces are initially filled with water, it has been hypothesized that after the CO_2 have been underground for hundreds to thousands of years, chemical reactions will dissolve some or all of CO_2 in the saltwater, with some fraction converted to carbonate minerals, thus becoming part of rock itself (Gunter et al. 2004). These are generally termed as secondary trapping mechanisms that continue to increase storage security over time, and have been the subject of significant research over the years (Benson and Cole 2008).

Another proposed mechanism for trapping CO_2 is the so called solubility trapping in saline aquifers, which is dependent on pressure, temperature, and the salinity of the brine (Koschel et al. 2006). Under typical geological formation storage conditions, the solubility of CO_2 in brine ranges from 2 to 5% by mass, and the laboratory studies have indicated that dissolution of CO_2 tend to be rapid at high pressure when water and CO_2 share the same pore space (Holloway 2008). However, in real injection system, the dissolution of CO_2 could be limited by the variability of contact area between CO_2 and the fluid phase. Solubility trapping decreases the amount of CO_2 subject to buoyant forces that drives CO_2 upwards.

The third type of secondary trapping is the ‘mineral trapping’ which occur when acidic brines enriched with CO_2 react directly or indirectly with minerals in the geologic formation, leading to precipitation of stable secondary carbonate minerals (Gunter et al. 2004). This mechanism generally traps CO_2 permanently, although significant degree of mineral trapping could take several thousands of years due to silicate mineral dissolution and carbonate mineral precipitation. Hence the impact of mineral trapping may not be realized until far in the future. In addition, the amount of CO_2 trapped by this mechanism is dependent on mineralogical makeup of the storage reservoir rock. For example, rocks with large fraction of feldspar minerals are expected to have significant amount of mineral trapping, while quartz-dominated reservoirs have little or no mineral trapping. Secondary trapping mechanisms are not substitute of high-quality seal, however, they do act over decadal to millennial timescales thereby increase the CO_2 storage security over time, and their relative importance will change over time depending on hydrogeological attributes of the storage site, such as mineralogy multiphase fluid flow properties stratigraphy and structural formation.

13.7.2 Issues Associated with Carbon Dioxide Storage

The ability to scale-up the existing operations is the central among the issues to be resolved before CCS can emerge as a viable option for global CO_2 emission reduction. Therefore, if CCS is to be implemented and have impact on CO_2 emission reduction, at least 20- to 25-fold increase in the amount injected underground will be required annually for CO_2-EOR today. It will also require an infrastructure on the scale of current oil industry. The ability to scale up the existing operations is central among the issues to be resolved before CCS can be considered as one of the viable option for the global CO_2 emission reduction. Achieving such a scale-up relies on several factors, including storage capacity, injectivity, risk management to avoid detrimental environmental impacts such as groundwater pollution, induced seismicity, and ecosystem degradation, as well as availability of intervention methods to remediate unanticipated leakage of CO_2 or other unintended and unplanned events (Table 13.3).

Table 13.3 Risks of CO_2 storage, environmental impacts and risk management approaches

Environmental risk	Impacts	Management
Leakage of CO_2 into the atmosphere	Lack of effectiveness of CCS	Proper site selection, effective monitoring, remediation of leakage pathways
Underground leakage and accumulation of elevated concentrations of CO_2 in ecosystems	Damage to CO_2 sensitive habitats	Proper site selection, monitoring of soil gas, remediation of leakage pathways and ecosystem cleanup
Exposure of high CO_2 to humans	Chronic or acute health concerns from CO_2 exposure	Proper site selection, monitoring, controlled access, remediation of leakage pathways
Leakage of CO_2 into groundwater	Acidification of groundwater and potential dissolution of toxic minerals	Effective site selection, monitoring of groundwater quality, restrict groundwater use if contaminated, remediation of leakage pathways
Leakage of hydrocarbon into groundwater	Contamination of groundwater with hydrocarbon compounds	Proper site selection, monitoring of groundwater quality, restricted use of contaminated water, remediation of leakage pathways, groundwater cleanup
Displacement and leakage of saline brine into drinking water aquifers or surface water	Contamination of groundwater or surface water with dissolved salts	Proper site selection, monitoring of groundwater quality, restricted use of contaminated water, remediation of leakage pathways, groundwater cleanup
Induced seismicity	Potential structural damage as well as felt ground motion	Proper site selection, monitoring of both pressure and seismic activity, limit pressure buildup

13.7.2.1 Permanence of Geologically Stored Carbon Dioxide

One of the key questions for the geologic CO_2 storage is how long the CO_2 will remain trapped underground? Several lines of evidence have suggested that for a well-selected and managed storage formations the retention rates may be high and more than sufficient for the purpose of avoiding CO_2 emissions into the atmosphere. These specifically include: (i) natural oil, gas, and CO_2 reservoirs that have demonstrated the buoyant fluids such as CO_2 can be trapped underground for millions of years, (ii) industrial analogues such as gas storage, CO_2-EOR, acid gas injection, liquid-waste disposal operations that have developed methods for injecting and storing fluids without compromising the integrity of caprock or storage formation, (iii) geochemical processes that can contribute to long-term CO_2 retention—such as physical CO_2 trapping beneath low permeability or impermeable rocks, dissolution of CO_2 in the brine, capillary trapping of CO_2, adsorption on unmineable coal, and mineral trapping. Overall, these trapping mechanisms increase the security of storage over time, and minimizes potential leakage of CO_2 to the land surface, (iv) experiences gained from projects which had large amount of monitoring data, such as Sleipner Project in North Sea and Weyburn Project in Saskatchewan, Canada has demonstrated a high degree of CO_2 containment so far.

Overall, the permanence of geologic sequestration depends on the combined effectiveness of several physical and chemical mechanisms that combine to trap this supercritical CO_2. In general, CO_2 is less dense than the saline groundwater it displaces in the pore space of the rock formations where it is injected. It will therefore, rise buoyantly until trapped beneath an impermeable barrier, or seal formed by a stratigraphic or other structural discontinuity. This physical trapping mechanism is comparable to the natural geologic trapping of oil and gas and can theoretically retain fluids for thousands to millions of years. CO_2 that is not physically trapped in this manner may escape through leakage pathways or it may migrate slowly through the rock pore space and become trapped as a residual fluid held in place by molecular surface tension (Ide et al. 2007). It is expected that some of the injected CO_2 will eventually dissolve in groundwater (brine), and some may be trapped in the form of carbonate minerals formed by chemical reactions with the surrounding rock (Kharaka et al. 2006a). However, all of these processes are susceptible to change over time after CO_2 injection (Hovorka et al. 2006), necessitating long term monitoring during and after the injection has stopped.

In general, the physical trapping mechanisms are viewed as more important over short timescales (a few decades); the relative importance of chemical dissolution and mineral reactions increases over time scales of centuries to thousands of years (Benson et al. 2005; Benson and Cole 2008). Because the permanence of geologic sequestration is one of its principal benefits, there is a critical need to understand the potential for leakage of injected CO_2 back to the atmosphere. Faults, fractures, and stratigraphic discontinuities may offer pathways for CO_2 leakage. Many potential structural traps are known in areas where oil and gas have been extracted, and CO_2 injection can enhance oil recovery, so these areas tend to be preferred sequestration injection sites. Unfortunately, these areas are also perforated by existing or abandoned wells that may act as conduits for leakage (Bachu and Celia 2009; Gasda et al. 2004).

The injection process itself may affect the geomechanical integrity of trapping structures (Hawkes et al. 2005). Valuable information about potential leakage can and have to be gathered in studies of natural geologic analogs of CO_2 storage and venting (Fessenden et al. 2009; Heath et al. 2009; Evans et al. 2001). However, many aspects of geologic CO_2 sequestration have no typical natural analogs, and therefore, much of the existing understanding has been learned from ongoing commercial-scale demonstrations of CO_2 sequestration operations such as those in Sleipner, Norway and Weyburn, Saskatchewan and In Salah, Algeria (Arts et al. 2008; Mathieson et al. 2011; White 2009), and other smaller pilot projects such as Frio, Texas, USA, Illinois, USA, Japan and others (Hovorka et al. 2006, 2013; Picard et al. 2011). Sequestration field tests at smaller scales have also become a primary venue for learning how to monitor and anticipate the fate of injected CO_2 (McPherson 2009; DOE 2012). Numerical models are an essential tool for understanding the complex interactions among the many factors that control fluid chemistry and transport. Models of geochemical interactions, multiphase fluid transport, and the combined effects of geochemistry and transport have been widely utilized to model the reservoir conditions and reaction properties (Gunter et al. 1997; McPherson and Cole 2000; White et al. 2005; Kaszuba and Janecky 2009). However, the uncertainties in model simulations must be quantified (Zerai et al. 2009) to provide meaningful assessments of risk. A wide range of scientific and engineering expertise is required for understanding the permanence of geologic CO_2 trapping mechanisms over the full range of potential storage time scales (Doughty and Myer 2009; McPherson 2009).

13.7.2.2 Storage Capacity

Just as the potential global amount of terrestrial C sequestration is limited by available land area, the global capacity for geologic carbon sequestration is constrained by the pore volume and distribution of potential storage sites. One frame of reference for geologic storage of injected CO_2 is to compare the volume of extracted fuels to the volume of injected CO_2 produced by combustion of equivalent fuel volumes. Generally, the combustion of oil and bituminous coal produces volumes of compressed supercritical CO_2 that exceed the volume of extracted fuel by factors of three and four, respectively, while the combustion of natural gas produces a nearly equal volume of compressed CO_2. In addition, the storage of CO_2 in dissolved form requires saline groundwater volumes many times larger than the volumes of the extracted fuels. Therefore, the potential underground CO_2 storage capacity needed is much greater than the vast existing operations of the fossil fuel industries. The large difference between the volume requirements of compressed and dissolved CO_2 is one source of uncertainty in estimates of global geologic sequestration capacity. An analysis (Dooley et al. 2006) suggests that the global storage capacity of physical traps associated with depleted oil and gas reservoirs is about 220 Pg C. The potential global storage capacity of deep porous rock formations that contain saline groundwater is much larger, and estimated to be approximately 3000 Pg C (Dooley et al. 2006). However, these formations are not as well-characterized as oil and gas reservoirs, and less is known about the effectiveness of trapping mechanisms at these sites. Unmineable coal beds have also been proposed for potential CO_2 storage, particularly in conjunction with coalbed methane recovery (Gunter et al. 1997). Overall, the global capacity estimates of geologic CO_2 sequestration remains a challenge because of the many differences in assumptions and the calculation methods. Most recent estimates provide an upper bound on the CO_2 storage capacity of sedimentary basin ranging from 5000 to 25,000 Pg CO_2 (Benson et al. 2012). Oil and gas reservoirs are anticipated to have a storage capacity of an order of 1000 Pg CO_2 (Benson et al. 2012), but, these reservoirs are limited geographically to hydrocarbon-rich regions of the world, and oil and gas reservoirs may not be available until oil and gas are fully depleted or until market conditions favor CO_2-EOR. Saline aquifers are assessed to have largest storage capacity with the global estimates ranging from 4000 to 23,000 Pg CO_2. There is a limited experience for assessing effectiveness and safety of saline aquifers storage, however. Also the uncertainty persists about how much of the estimated large storage potential can actually be utilized (Juanes et al. 2010; Bradshaw et al. 2007; Ehlig-Economides and Economides 2010). A 500-fold scale up of the existing saline aquifer storage project would be required for Pg scale storage. Unmineable coal beds are considered to have low storage potential.

Standardization and transparency of capacity assessment methodologies are needed so that improved estimates of the potential effectiveness of geologic CO_2 sequestration compared to current and future CO_2 emissions can be assessed (Bachu et al. 2007; DOE 2012; Burruss et al. 2009; McPherson 2009). To fully assess the potential for geologic carbon sequestration, economic costs and environmental risks must also be taken into account. Many of the factors affecting geologic CO_2 sequestration depend on local conditions, and will vary according to the type of storage formation. The depleted oil and gas reservoirs are generally well characterized and are less prone to unknown risks. However, they are of limited in capacity and geographic distribution, and may require greater proportional investment in infrastructure. The potential capacity of formations containing saline water is larger and more widely distributed, but few of these formations are well-characterized, leading to large uncertainty in capacity estimates. Unmineable coal beds may have the advantages of proximity to large power plants and CH_4 recovery, but their storage characteristics may be poorly characterized, and also potential future coal and natural gas resources may be rendered unusable by CO_2 storage.

13.7.2.3 Pressure Build up, Injectivity and Induced Seismicity

When CO_2 is injected into a storage reservoir, the pressure increases due to combination of viscous forces associated with multiphase flow of CO_2 within the plume and displacement of in situ fluids (Nordbotten et al. 2005). The magnitude of pressure buildup depends primarily on the permeability and thickness of the storage reservoir and the injection rate. In the case of sealed reservoir (i.e., sealed on the top, bottom, and sides), pressure also increases due to compression of pore—filling fluids (Zhou et al. 2008). Monitoring of pressure buildup and associated geochemical effects are needed for CO_2 storage projects. Concerns over how much excessive pressure buildup limits storage capacity in saline aquifers (Ehlig-Economides and Economides 2010) and induced seismicity (Zoback and Gorelick 2012) have raised concerns among researchers. However, some researchers have argued that these concerns are misplaced for the existing million-tonnes CO_2 yr^{-1} injection projects (Cavanagh et al. 2010). Some techniques for pressure management include (i) injection rate control (Birkholzer et al. 2009), and (ii) brine extraction (Birkholzer et al. 2009). Overall, pressure buildup is a manageable issue (Chadwick et al. 2010).

Injection of CO_2 into saline aquifers could lead to slip along preexisting faults and to associated seismicity (Zoback and Gorelick 2012). In general, induced seismicity is gaining attention with disposal of wastewater from hydraulic fracturing operations for shale gas development in the United States (Frohlich 2012) and natural gas extraction in the Netherlands. Researchers are actively investigating whether and how much induced seismicity is a constraint to CO_2 storage and how to manage injection operations to avoid it. There is a need for research to establish the extent of induced seismicity and its potential limitation for CO_2 injection, as well as how to manage the injection operations to avoid it.

13.7.2.4 Other Issues Associated to Carbon Dioxide Injection

Other risks include deformation of the land surface (Jung et al. 2013), contamination of potable water supplies, and adverse effects on ecosystems and human health. Numerous regulatory issues also affect the implementation of geologic sequestration, including determination of rules affecting injection wells, post-injection ownership, and liability across multiple jurisdictions and even among different countries. As with terrestrial sequestration, geologic sequestration cannot be accomplished in isolation from a broad range of environmental and societal concerns (Sundquist et al. 2008).

13.8 Risks of Geological Storage of CO_2

Two broad categories of risks of CO_2 storage can be identified: (1) risks associated with the release of CO_2 back to the atmosphere, and (2) health, safety, and environmental risks associated with the local impacts of storage operations and potential leakage out of storage reservoir. The consequences of release of CO_2 back to atmosphere are that the CCS may be less effective as a mitigation measure than the anticipated. Also there could be financial liabilities associated in buying credits and also assuming the responsibility for those emissions. Overall, the risks of release of CO_2 to the atmosphere are the greatest during the period of CO_2 injection, which for any particular project are limited to several decades. Legal and administrative mechanisms for managing long-term liabilities beyond the period of operation and post-injection assurance monitoring are currently under development by government agencies worldwide. The health, safety, and environmental concerns of CO_2 storage are similar to those generally associated with oil and gas fields—such as habitat fragmentation, infrequent uncontrolled release from wells, noise, as well as road traffic. Additionally, if CO_2 or brine leaks out of storage reservoir, it could affect groundwater quality and result in locally hazardous concentrations of CO_2 in the air. It can also cause micro-seismicity if injection pressures are very high.

Based on existing scientific understanding of the processes controlling CO_2 migration in the subsurface, CO_2 should remain securely stored in the geological formations for thousands of years or longer if these conditions are met: (i) the seal has low permeability and high capillary pressure to prevent migration into the seal, (ii) CO_2 cannot migrate around the edge of the seal or through breaches in the seal caused by leaking wells, faults, or fractures, (iii) the injection pressure is low enough to avoid fracturing the seal (Benson et al. 2012). Although these principles are clear and straightforward, the main challenge is to identify sites that meet these conditions, since the subsurface geology is naturally complex, and geological storage sites are by necessity large, with CO_2 plumes potentially covering hundreds of km^2 area, and this makes it harder to assess the security of storage.

Although CO_2 is generally non-toxic inert gas, exposure to concentrations in the excess of several percent can lead to adverse consequences, particularly since CO_2 is denser than air, hazardous situations arise when large amount of CO_2 accumulate in low-lying confined or poorly ventilated spaces. If large amounts of injected CO_2 escape from a storage site, it could present risks to health and local environment. However, hazardous conditions would only persist several hundred meters from the site of release (Aines et al. 2009). Such large release could be associated with surface facilities, injection wells, or leakage which remained unchecked, and could impact groundwater and ecosystems. Persistent leaks could suppress respiration in the root zone or result in soil acidification and leading to tree kills. Tree kills have been observed at the soil gas concentration in the range of 20–30% at Mammoth Mountain in California caused by volcanic outgassing of CO_2 which has been occurring for several decades (Martini and Silver 2002).

Potential local health, safety, and environmental concerns from geological storage include: (i) occupational risks associated with well and field operations, (ii) leakage of CO_2 or brine out of storage and migration to drinking water aquifers, (iii) resource damage near well head due to unwanted CO_2 migration into nearby mineral resources, (iv) ecosystem impacts in the event that CO_2 is released into soil, wetlands or surface waters, (v) public safety risks from exposure to elevated CO_2 concentrations if CO_2 is released at the surface, and (vi) structural damage associated with land surface deformation or microseismicity. Overall, the extensive experience with CO_2-EOR and injection of CO_2 in the ongoing demonstration projects in general indicates that risks from geological CO_2 storage facilities are manageable using standard engineering controls and procedures. The highest risk event that could occur in CCS is loss of well control which is infrequent.

13.9 Monitoring and Risk Management

Monitoring play a key role to observe the behavior of the injected CO_2, calibrate and validate predictive models and provide any early warning that leakage may be imminent, so that remediation measures such as plugging abandoned wells can be implemented. The regulatory oversight capacity is also needed to ensure due diligence for site selection, engineering, operation, monitoring, verification, and necessary remediation for CO_2 storage project if needed. Combination of monitoring techniques—e.g., geophysics, hydrology, and geochemistry that monitor injection rates and pressure, tracks migration of the CO_2 plume, detect leakage out of storage reservoir, and detect microseismic activity are available from a variety of other applications including oil and gas industry natural gas storage disposal of liquid hazardous waste in deep geological formation, groundwater monitoring, food preservation and beverage industries, fire suppression, and ecosystem research. These techniques have been adapted for use in CO_2 sequestration monitoring. Monitoring has been a key element of the industrial scale storage projects (Arts et al. 2008; Mathieson et al. 2011; White 2009). Most of these techniques have also been demonstrated at small-scale pilot projects around the world (Hovorka et al. 2006, 2013; Jenkins et al. 2012; Martens et al. 2012).

Geophysical monitoring methods can be used to monitor the location of CO_2 plume (Arts et al. 2008; Sato et al. 2011; Couëslan et al. 2013). Seismic imaging can detect compressional wave velocity and attenuation caused by the presence of separate phase CO_2 (Couëslan et al. 2013). Electromagnetic imaging can detect decrease in electrical conductivity in the pore spaces of the rock, while gravity measurements detect decrease in bulk density of the rock caused by presence of CO_2 (Bergmann et al. 2012). Seismic methods for monitoring have been used successfully at Sleipner, Weyburn, the Frio Brine Pilot and Otway Basin Pilot projects and others (Arts et al. 2008; Hovorka et al. 2006; White 2009; Pevzner et al. 2011). Geochemical measurements are generally deployed in two types:

(i) direct techniques—including measurement of brine chemistry and introduced or natural tracers in samples obtained from injection horizons in observation wells, (ii) monitoring the near-surface for possible CO_2 leakage in the immediate vicinity of injection and observation wells, and also from soils and shallow groundwater wells within the injection area. Most of geochemical methods have been used primarily for the pilot scale tests due to the insights they provide, which is important in understanding the interactions between CO_2 and the storage reservoir rocks and fluids (Kharaka et al. 2006a, b). They have also been used extensively at the Weyburn Project (Emberley et al. 2005) and the Illinois Basin Decatur Project (Ussiri, Personal communication). They include: pH, alkalinity, soil gas compositions, and the stable isotope geochemistry, among others. The most diagnostic indicator of brine-CO_2 interactions which indicates breakthrough of CO_2 to monitoring wells is pH. Enrichments of metal constituents compared to pre-injection are indicators of mineral dissolution reactions occurring at depth during brine-CO_2 rock interactions (Emberley et al. 2005; Kharaka et al. 2006a, b). Monitoring of surface fluxes can also directly detect and measure leakage. Surface CO_2 fluxes can be measured directly with eddy covariance towers, flux accumulation chambers and field-portable high-resolution infrared (IR) gas analyzers (Lewicki et al. 2007, 2009; Lewicki and Hilley 2009; Spangler et al. 2010). Much progress has been achieved to quantify and improve detection levels and also increase the number of available surface monitoring of CO_2 leakage techniques (Spangler et al. 2010; Krevor et al. 2010).

13.10 Bioenergy Coupled with Carbon Dioxide Capture and Storage (BECCS)

Bioenergy coupled with CCS (BECCS) (Liu et al. 2011) can mitigate climate change through negative emissions if CCS can be successfully deployed (Cao and Caldeira 2010; Creutzig et al. 2015). BECCS or Bio-CCS is defined as a process in which CO_2 originating from biomass is captured and stored. It can be through energy production process or any other industrial process with CO_2-rich process streams originating from biomass feedstocks. BECCS has a potential for negative emissions which can also compensate for emission from other sectors, especially transport. BECCS is markedly different from fossil CCS because it reduces CO_2 emissions by storing CO_2 in long-term geological sinks while continually sequestering CO_2 from the air through regeneration of biomass resource feedstock. An example of BECCS is the Illinois Basin-Decatur Project, a demonstration project that captures CO_2 from ethanol fermentation and inject it into Mount Simon geological formation—which is projected to store 1 Mt CO_2 yr^{-1} (Gollakota and McDonald 2012). In addition to risks associated with CCS, bioenergy production could reduce C stocks through land use conversion, land disturbance through tillage. Similarly, use of inorganic fertilizer in bioenergy crop production such as corn production for ethanol causes increased N_2O emissions. Therefore, lifecycle analysis is needed to evaluate the mitigation potential of BECCS.

13.11 Oceanic Sequestration

During 2006–2015, world's oceans accounted for a global net uptake of about 2.6 ± 0.5 Pg C yr^{-1} which occurs naturally through chemical reactions between dissolved inorganic carbon in the ocean surface and the increasing CO_2 concentration in the atmosphere (Le Quéré et al. 2015, 2016). This natural ocean uptake of CO_2 was a primary interest of Roger Revelle when he described the "large-scale geophysical experiment" more than 50 years ago. The oceans will continue to be the primary long-term sink for anthropogenic CO_2 that is not sequestered by other means. The chemical reactions between atmospheric CO_2 and the ocean surface occur rapidly, and over time any absorbed CO_2 is mixed downward throughout the oceans. Over the geological time scales, increases in atmospheric CO_2 concentration has, and will be attenuated in this way by ocean-surface equilibration and mixing with the entire global ocean volume. The global capacity of this natural sequestration mechanism is considered to be large. For example, the oceans could absorb approximately 1000 Pg C while maintaining equilibrium with present-day atmospheric CO_2 levels (Kheshgi et al. 2005; Caldeira et al. 2005). This capacity could also be enhanced by chemical reactions between dissolved CO_2 and marine carbonate sediments. However, the rate of ocean mixing limits natural ocean CO_2 absorption to a pace that cannot match the rate of anthropogenic CO_2 production through fossil fuel combustion and industrial processes.

The long-term mixing and equilibration of ocean and atmospheric CO_2 assures that any proposed deliberate injection of CO_2 into the deep ocean, although potentially sequestering the CO_2 for a period of perhaps centuries, would eventually equilibrate with the atmospheric CO_2. Therefore, permanence of ocean CO_2 sequestration remains questionable. Nevertheless, injection of CO_2 into the oceans requires capture technologies and infrastructure similar to those described above for geologic CO_2 sequestration. In typical ocean temperatures, injected CO_2 will be in liquid form at depths greater than 400–500 m. At high concentrations, the liquid CO_2 may also form a solid hydrate phase. At depths greater than 3000 m, the liquid CO_2 generally becomes compressed to a density greater than that of the surrounding seawater. These properties have led to various suggestions for pumping CO_2 into the oceans at rates sufficient to mitigate rising atmospheric CO_2 levels and to reduce the peak concentrations expected without mitigation in the next century (Caldeira et al. 2005; Adams and Caldeira 2008). For example, it has been proposed that liquid CO_2 could be injected into sediments beneath the deep sea floor (House et al. 2006). However, in addition to permanence, a significant deterrent to oceanic CO_2 sequestration is the growing evidence for negative impacts of acidification caused by the chemical reactions that occur when CO_2 is dissolved in seawater (Feely et al. 2009). Many marine organisms and ecosystems that depend on the formation of carbonate skeletons and sediments that are vulnerable to dissolution in acidic waters will be impacted. Laboratory and field measurements indicate that CO_2-induced acidification may eventually cause the rate of dissolution of carbonate to exceed its rate of formation in these ecosystems. The impact of ocean acidification on coastal and marine food webs and other resources are poorly understood, however (Guinotte and Fabry 2008; Hoegh-Guldberg and Bruno 2010). In addition, many unanswered environmental uncertainties have deterred proposals to enhance the ocean CO_2 uptake by fertilization of marine ecosystems (Buesseler et al. 2008; Adams and Caldeira 2008). Also, as with other CO_2 sequestration methods, the implementation of oceanic sequestration requires consideration of wide-ranging economic, environmental, social and political constraints. As a result, only minimal research efforts have been implemented in ocean CO_2 sequestration.

13.12 Geochemical Sequestration

Due to the urgency of mitigating the effects of anthropogenic CO_2 emissions and the associated many constraints on implementing CCS at the impactful level or ocean CO_2 sequestration, some scientists have pressed for broad consideration of novel approaches to global carbon cycle management (Cicerone 2006; Broecker 2007). Some of the approaches include geochemical methods that mimic the long-term cycling of CO_2 through the Earth's crust (Lackner 2002). CO_2 forms carbonic acid in water, and reacts on land with carbonate and silicate minerals during chemical weathering to liberate dissolved bicarbonate and carbonate ions. These ions are transported by rivers and streams to the oceans, where they combine with dissolved calcium and magnesium to form carbonate minerals that accumulate in sediments and thus are returned to the Earth's crust. Geochemical sequestration occurs when these reactions lead to net accumulation of carbon in dissolved or mineral form. Their natural geologic effectiveness is conspicuous in the large amounts of carbon dissolved in the oceans and retained in limestones and other carbonate sediments. Deliberate geochemical sequestration involves the acceleration of natural weathering and burial processes. Geochemical methods have been suggested for increasing the rates of weathering of silicate minerals (Lackner et al. 1997; Lackner 2002) and carbonate minerals (Rau and Caldeira 1999), thereby increasing geochemical CO_2 sequestration. Some proposals focus on the accelerated formation of carbonate minerals (i.e., mineral carbonation), which are generally more stable than the combination of silicate and dissolved CO_2 reactants (McGrail et al. 2006; Oelkers et al. 2008). A particularly creative idea is the addition of alkalinity to ocean surface waters, which would enhance natural ocean uptake of atmospheric CO_2 while buffering ocean acidification (Kheshgi 1995). Although high costs and slow rates of reaction make geochemical sequestration less attractive now than many alternatives, this option certainly merits further investigation and discovery during the current period of nascent carbon cycle management (Stephens and Keith 2008).

13.13 Conclusions

CCS involves the integration of four elements—CO_2 capture, compression, transportation to the storage location, and isolation from the atmosphere by pumping it into appropriate geological formations such as saline aquifers, exhausted oil and gas reservoirs and coalbeds with effective seals to keep it safely and securely trapped underground and isolated from the atmosphere. Storage in other rock types such as basalt, oil and gas shales, and sea bed sediments may also be possible, but much less is known about their potential. Technologies for CCS are at different stages of development, some such as CO_2 compression, or CO_2-EOR is fully mature, while some such as storage in saline formations are in early stages of demonstration. Three approaches are available for capture from power plants and industrial sources that produce CO_2 gas with relatively low concentration of contaminants. These are pre- and post-combustion capture, and oxy combustion capture. Both processes have been routinely used for other applications but their optimization with power plants or most industrial processes have not been fully achieved. Considering full life cycle emissions, CCS technology can reduce up to 65–85% of CO_2 emissions from fossil fuel combustion from stationary source. Small-scale and industrial demonstration projects have provided insights into the feasibility of CCS technologies. Researchers have gained experience in industrial-size demonstration projects that have been running safely for years such as Sleipner in Norway and Weyburn in Canada. Additionally, decades of CO_2-EOR in North America have contributed in added knowledge base. Small-scale geological storage experiments aided by laboratory experiments and modelling has also contributed in development of improved monitoring and performance prediction tools. Nevertheless, costs of CCS implementation have remained prohibitive because of other price factors. Despite the advances in science and technology of CCS, the future of CCS is highly uncertain, and the past decade has shown how dependent the technology is on social, political, and financial context. The financial crisis of 2008, and lack of commitment from Copenhagen climate change conference in 2009, as well as the rise of shale gas in United States, lower cost of renewable energy, a public that has remained skeptical about the role of CCS in mitigating climate change, and rising resources costs have all contributed to diminishing attention to CCS, leading to cancellation of various planned demonstration projects and low investment in the CCS in recent years. Action on climate change at national and/or international either through pricing C, mandating technology on a sectoral basis while also imposing emission standards requires political leaders to make clear choices and commitment against a high C future. There is also a need to assure the public that geological storage of CO_2 is safe and an effective means to stabilize and in the long-run to reduce atmospheric CO_2 concentration. But credible, accessible, and scientifically sound information sources, appropriate engagement activities are currently lacking, and this has led to lack of community support for CCS. Successful experiences from CO_2-EOR, and ongoing small scale and industrial scale demonstration projects demonstrate that at least on this limited scale, appropriately selected and managed geological reservoirs likely retain nearly all the injected CO_2 for long time and provide the benefits for intended purposes of CCS. However, up to tenfold scale-up in size of current individual industrial scale demonstration would be needed to capture, transport, and store emissions from a large-scale point source such as 500–1000 MW coal-fired power plant, and a thousand-fold scale-up in size of current CCS projects would be needed to reduce CO_2 emissions at the level of Pg C yr^{-1}. This remain a big challenge which need to be addressed. Specifically, is there sufficient capacity to store these quantities of CO_2? At what cost? Does institutional, economic, and technical constraint to implement CCS on this scale be overcome? The answers to these questions, together with social acceptability will determine the future success of CCS.

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