Chapter 9

Carbon Dioxide, Other Greenhouse Gases, and the Carbon Cycle

Abstract The physical and chemical properties of carbon dioxide are essential for the existence of humankind on Earth because of its role in the greenhouse effect. Water vapor, methane, and nitrous oxide are also important greenhouse gases as they help keep the planet warm. The carbon cycle is important for life on Earth because life is carbon based. An illustration in this chapter shows how carbon moves through the environment. Sources and sinks of several of the greenhouse gases are discussed. The ozone hole is discussed with its ramifications for causing harm to life forms. Global Warming Potentials (GWPs) are defined relative to CO_2. Other greenhouse gases are discussed.

Keywords Halocarbons • Methane • IPCC • Dry ice • Keeling • GtC • Dry ice • ENSO • GWP • TOA • Carbon • Cycle • GPP • SAR • ESRL • Gigatonne • Source • Sink • Clathrate • Disequilibrium • Ice core • Montreal Protocol • Nitrous • Oxide • Oxidation • Reduction

Things to Know

The following is a list of things to know from this chapter. It is intended, as it is in each chapter, to serve as a guide to points of emphasis for the student to keep in mind while reading the chapter. Before finishing with this and every chapter, the "Things to Know" should be understood and can be used for review purposes. The list may not include all of the terms and concepts required by the instructor for this topic.

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Things to Know

0.040%
Halocarbons
Laughing Gas
1991 Eruption
Clathrate Gun Hypothesis
Nitrous Oxide GWP
Nitric Oxide
GtC
GWP
CFCs
Dry Ice
Keeling Curve
Sinks of Carbon Dioxide
Sources of Carbon Dioxide
Reservoir Sizes of Carbon Dioxide in GtC per Year
−109.3°F
Ozone Hole
Carbon Dioxide Trends in the Atmosphere
Carbon Cycle Equilibrium
IPCC
Hydroxyl Radical
2.36 ppm
SAR
CO_2
Sinks of Methane
Mt. Pinatubo
IR
Carbon Dioxide
Carbon Cycle
ENSO
Global Warming Potential
UV
CH_4
Sources of Methane
Greenhouse Gases
350 ppm or Less
TAR
1.9 ppm per Year

9.1 Introduction

Greenhouse gases remained in fairly constant concentrations until the Industrial Revolution beginning around the middle of the eighteenth century. Beginning in the mid-1700s these gases, carbon dioxide, methane, and nitrous oxide show a constantly increasing concentration in the atmosphere accelerating in the later twentieth and early twenty-first centuries. There is little doubt that these increases are mainly derived from humankind's burning of fossil fuels. The illustration below (Fig. 9.1) shows that the atmospheric concentrations of three greenhouse gases were relatively stable in the atmosphere until the eighteenth century when they began to increase rapidly in concentration.

9.2 Carbon Dioxide (CO_2)

Carbon dioxide (CO_2) is an extremely important greenhouse gas as we've seen in earlier sections of this text, especially in Chap. 8. Carbon dioxide is a greenhouse gas that transmits visible light but absorbs strongly in the infrared and near-infrared, before slowly re-emitting the infrared at the same wavelength as that which was absorbed. It is a very small percentage of the total atmosphere (0.040%) and because of this it is difficult for some to recognize its importance as a major heat-trapping substance.

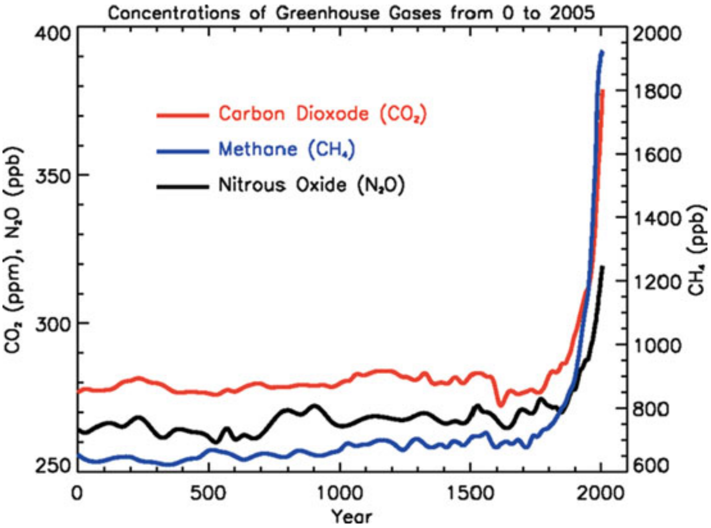

Fig. 9.1 Atmospheric concentrations of important long-lived greenhouse gases over the last 2,000 years. Increases since about 1750 are attributed to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb), indicating the number of molecules of the greenhouse gas per million or billion air molecules, respectively, in an atmospheric sample (From IPCC AR4 2007)

Carbon dioxide and water vapor are the two most important greenhouse gases as they readily block infrared (IR) radiation from escaping to the stratosphere and outer space. This heat energy is what keeps the Earth warm enough for life to exist and thrive. How do these compounds accomplish this? Let's look at carbon dioxide first.

One way to look at how greenhouse gases work in the atmosphere is to consider an analogy to the way an automobile's interior heats rapidly in sunlight. Glass acts as an absorber of both UV and IR waves. One can sit in an enclosed car in the sunlight and not get sunburned because of the absorption of UV rays by the windshield and windows in the car. One sitting in the car can also realize the rapid heating of the car's interior due to the blocking of the IR rays from escaping the enclosed interior of the car and keeping the heat inside. The windshield and windows act in a manner similar to greenhouse gases, allowing the UV rays to pass through them. Greenhouse gases trap heat inside the atmosphere as the glass traps heat inside the car. Visible light is let in but heat energy remains in the car. Greenhouse gases allow visible light in but block the flow of heat from escaping into space.

Carbon dioxide consists of three atoms, two of oxygen and one of carbon (CO_2). The atoms are held together by covalent bonds, that is, by a sharing of electrons. This allows the CO_2 molecule to vibrate in all three dimensions when agitated. Infrared radiation agitates the CO_2 molecule causing it to vibrate and absorb heat, then to re-radiate it in all directions as well as back to Earth's surface. This ability to absorb and then re-radiate heat is what makes the molecules of CO_2 and H_2O be effective greenhouse gases.

Carbon dioxide forms “dry ice” at −109.3°F. “Dry ice” is used to cool substances such as food and drinks in coolers but should not be used by humans in enclosed spaces. Carbon dioxide, like carbon monoxide, is denser than air and will displace the air in one’s lungs in a matter of a few hours in an enclosed air-tight space and cause suffocation and death.

During the last 250 years or so the absolute growth rate of CO_2 in the atmosphere has increased substantially; the first 50 ppm increase above the pre-industrial value was reached in the 1970s after more than 200 years, whereas the second 50 ppm was achieved in about 30 years. In the 10 years from 1995 to 2005 atmospheric CO_2 increased by about 19 ppm; the highest average growth rate recorded for any decade since direct atmospheric CO_2 measurements began in the 1950s. The average rate of increase in CO_2 determined by these direct instrumental measurements over the period 1960–2005 is 1.4 ppm per year. The rate of increase of carbon dioxide in the atmosphere in June 2012 stands at about 2 ppm per year.

The 2005 rate of increase of carbon dioxide in the atmosphere was 2.14 ppm year. The rate of increase is not steady from one year to the next but it is averaging around 2 ppm per year over the past several decades. For example, the Pinatubo volcanic eruption of 1991 slowed the increase for a few years. The massive release of sulfur dioxide during the eruption caused an increase in cloud cover which in turn resulted in cooling which then increased the dissolving of carbon dioxide in sea water. The resulting slight pause beginning in 1992 is visible in the Keeling Curve. The pause in the Keeling curve was canceled by an acceleration of CO_2 emissions in the next decade.

The Southern Oscillation also known as the El Niño-La Niña (ENSO) cycle also seems to have an effect on CO_2 levels in the atmosphere. The general trend, however, is unmistakable. The CO_2 concentration is increasing in the atmosphere and has been increasing for some time. And the rate of addition of carbon dioxide in the atmosphere is increasing.

The illustration shown in Chap. 4 in Fig. 4.4 is the solar radiation spectrum measured at the top of the atmosphere (TOA) and at sea level. Note the strong absorption bands for H_2O, CO_2, and O_3. Water vapor and ozone are compounds that absorb energy from the Sun as it passes through the atmosphere and also as it radiates back from the Earth’s surface. Carbon dioxide absorbs energy as it radiates back from the Earth’s surface.

9.2.1 The Keeling Curve

The Keeling Curve was introduced in the Introduction and is shown in Fig. 8.3. It illustrates the increase in atmospheric carbon dioxide from 1958 to the present (June 2012 at 396 ppm). Close examination of the curve will detect a dip in the curve beginning in 1992 as a result of the volcanic ash from the eruption of Mt. Pinatubo found its way to the stratosphere and resulted in a cooling of the planet for a couple

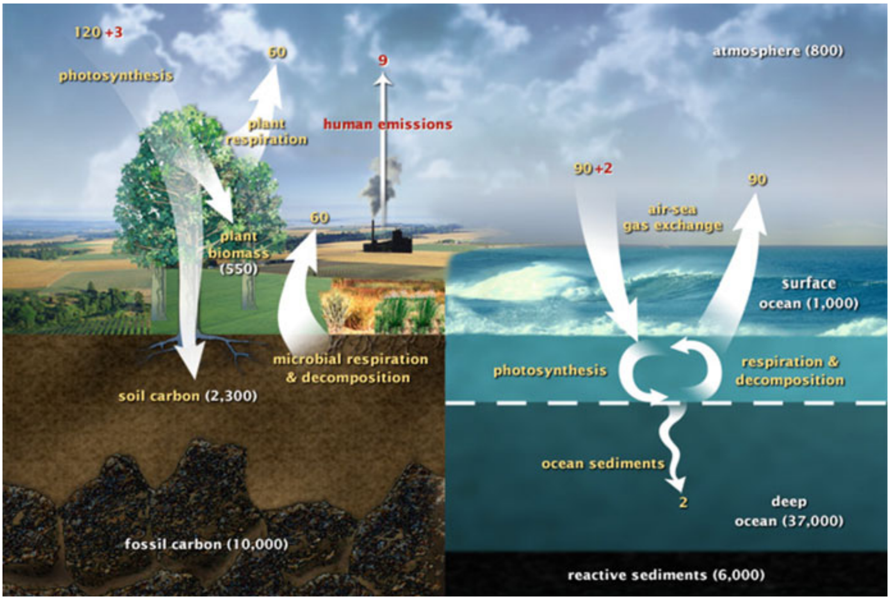

Fig. 9.2 The global carbon cycle showing the main annual fluxes in GtC year–1: pre-industrial 'natural' fluxes in *yellow* and 'anthropogenic' fluxes in *red* (Modified from Sarmiento and Gruber 2006, with changes in pool sizes from Sabine et al. 2004). The diagram of the carbon cycle shows the movement of carbon between land, atmosphere, and oceans in billions of tons of carbon per year. *Yellow* numbers are natural fluxes, *red* are human contributions in gigatonnes of carbon per year. *White* numbers indicate stored carbon (Based on IPCC AR4, WG1 Figure 8.3 by DOE and http://www.gfdl.noaa.gov/anthropogenic-carbon-cycle)

of years; again illustrating the correlation between Earth's temperature and carbon dioxide concentration in the atmosphere.

The curve shown in Fig. 8.3, as we saw in Chap. 8, was begun by C. David Keeling in 1958 at the Mauna Loa Observatory in Hawaii and is the longest continuous measurement of CO_2 in existence. Prior to Keeling's work, the correlation between rising carbon dioxide in the atmosphere and rising global temperature was not obvious. In fact, the rising carbon dioxide concentration in the atmosphere had been suspected due to the burning of fossil fuels, but it had not been scientifically documented, prior to the measurements by Keeling.

9.3 The Carbon Cycle

Carbon dioxide is an important link in the carbon cycle. The cycle is illustrated in Fig. 9.2.

The carbon cycle involves the movement of carbon through the Earth system pathways as follows:

- The atmosphere;
- The terrestrial biosphere, which is defined to include fresh water systems and non-living organic material, such as carbon in soil;
- The World Ocean, including dissolved inorganic carbon and living and non-living marine biota;
- The sediments including fossil fuels; and
- The Earth's interior, carbon from the Earth's mantle and rocks of the crust released to the atmosphere and hydrosphere by volcanoes and geothermal systems.

9.4 Carbon Dioxide and the Carbon Cycle

Carbon dioxide is part of the carbon cycle and as such should be in dynamic equilibrium with other things in the cycle, but it is not. There is an excess of carbon dioxide in the atmosphere as has been seen before in this text.

Figure 9.2 shows the carbon cycle with units of carbon in gigatonnes (1 gigatonne = 1 billion tonnes; GtC = gigatonnes of carbon). By far, the intermediate and deep ocean is the largest bank or reservoir of carbon on Earth, estimated at exceeding 37,000 gigatonnes of carbon in storage.

9.5 Sources and Sinks of Carbon Dioxide

Sources of carbon dioxide are such things as volcanoes, fumaroles, geysers, the burning of fossil fuels, conversion of methane, etc. Sinks of carbon dioxide are storage or areas that take up carbon dioxide such as the ocean, sediments, etc.

The movement of carbon, in its many forms, between the biosphere, atmosphere, oceans, and geosphere is described by the carbon cycle, illustrated in the diagram (Fig. 9.2). The carbon cycle is just one of the biogeochemical cycles but a very important one for life on the planet. Life on Earth of course is carbon based.

In Fig. 9.2, the natural or unperturbed exchanges (estimated to be those prior to 1750) among oceans, atmosphere and land are shown by the black numbers. The gross natural fluxes between the terrestrial biosphere and the atmosphere and between the oceans and the atmosphere are about 120 and 90 gigatonnes per year, respectively. Less than 1 gigatonne per year of carbon is transported from the land to the oceans via rivers either dissolved or as suspended particles. While these fluxes vary from year to year, they are approximately in balance when averaged over longer time periods. Additional small natural fluxes that are important on longer geologic time scales include conversion of organic matter from terrestrial plants into inert organic carbon in soils, rock weathering and sediment accumulation, and release from volcanic activity. The net fluxes in the 10,000 years prior to 1750, when averaged over decades or longer, are assumed to have been less than about 0.1 GtC per year.

Carbon dioxide has been increasing in the atmosphere at an ever increasing rate. The annual growth rate of atmospheric CO_2 was 2.36 ppm in 2010, one of the largest growth rates in the past decade. The average for the decade 2000–2009 was 1.9 ppm per year, 1.5 ppm for the decade 1990–1999, and 1.6 ppm for the decade 1980–1989. The 2010 increase brought the atmospheric CO_2 concentration to 396 ppm, 41% above the concentration at the start of the Industrial Revolution (about 280 ppm in 1750). The present concentration (400 ppm in June 2012) is the highest during at least the last 800,000 years and possibly in millions of years.

There is a difference in emitting carbon to the environment (in gigatonnes) and carbon dioxide (in gigatonnes) to the atmosphere and it is necessary to keep the two separate. In 2008, 8.67 gigatonnes of carbon were released from fossil fuels worldwide, compared to 6.14 gigatonnes in 1990. In addition, land use change contributed 1.20 gigatonnes in 2008, compared to 1.64 gigatonnes in 1990.

In the period 1751–1900 about 12 gigatonnes of carbon were released as carbon dioxide to the atmosphere from burning of fossil fuels, whereas from 1901 to 2008 the figure was about 334 gigatonnes. Humankind causes the emission of at least 30 gigatonnes of CO_2 per year to the atmosphere with 31.6 gigatonnes added to the atmosphere in 2011, according to the International Energy Agency (IEA).

Accumulation of atmospheric CO_2 is the most accurately measured quantity in the global carbon budget with an uncertainty of only about 4%. The estimated uncertainty in the global annual mean growth rate is about 0.1 ppm per year. The data are provided by the U.S. National Oceanic and Atmospheric Administration Earth System Research Laboratory (NOAA/ESRL) and include early data from the Scripps Institution of Oceanography (SIO).

Carbon is stored in Earth materials such as carbonates (limestone, dolostone, and chalk) and silicate rocks, as sediments, in the oceans, soils, vegetation, and in fossil fuels such as coal, natural gas, and petroleum products. When these materials break down as the result of chemical weathering, carbon is released to the environment, to the atmosphere, and the ocean.

The carbon cycle is one of the biogeochemical cycles. Carbon moves through the carbon cycle as follows:

- From the atmosphere to vegetation which uses CO_2 in photosynthesis to produce oxygen and water;
- From plants to soils and sediments;
- From fossil fuels to the atmosphere;
- From the atmosphere to the ocean;
- From the ocean to the atmosphere;
- From the surface of the ocean to deeper parts of the ocean;
- From animals to the atmosphere;
- From vegetation to animals;
- From chemical weathering (dissolution) to the ocean;
- From the burning of fossil fuels to the atmosphere and ocean.

Most of the carbon at present is moving from fossil fuels to the atmosphere and ocean and this has upset the natural equilibrium of the carbon cycle. Humans have

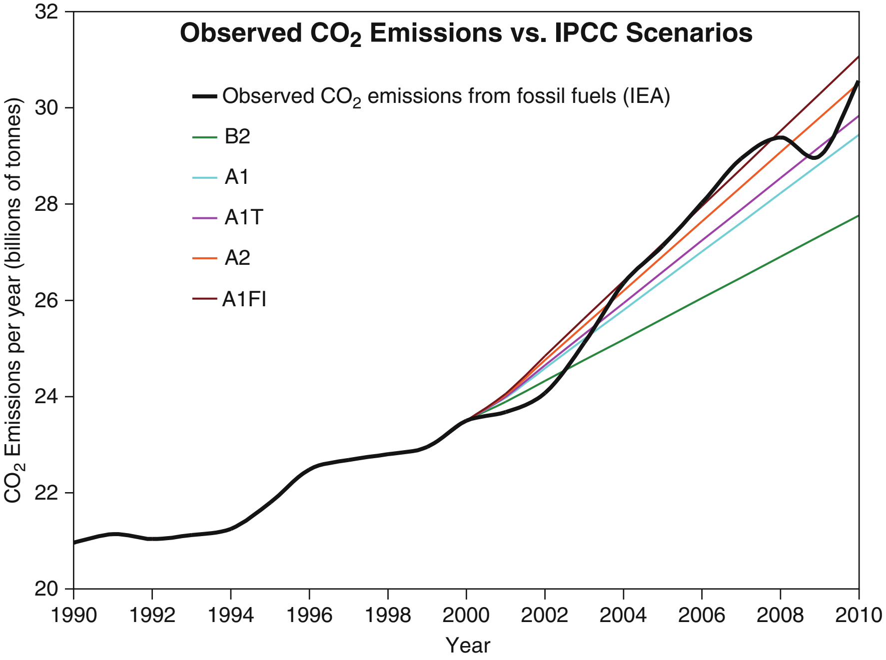

Fig. 9.3 U.S. Energy Information Administration (EIA) global human CO_2 annual emissions from fossil fuels estimates vs. IPCC SRES scenario projections. The IPCC Scenarios are based on observed CO_2 emissions until 2000, at which point the projections take effect

been altering the atmospheric parts of the carbon cycle by cutting down trees, raising crops, and burning fossil fuels. After thousands of years of equilibrium, the addition of carbon to the atmosphere and oceans by humans has upset this natural state so that we now have a major excess of carbon throughout the ecosystems of the planet.

Over the long term, the carbon cycle has seemed to maintain a balance that has prevented all of Earth's carbon from entering the atmosphere, as it does in the case of Venus, or from being stored entirely in rocks. This balance helps keep Earth's temperature relatively stable, like a thermostat until the thermostat is changed (Fig. 9.3).

This thermostat works over a few hundred thousand years, as part of a slow carbon cycle. This means that for shorter time periods, tens to a hundred thousand years, the temperature of Earth can vary. And, in fact, Earth swings between ice ages and warmer interglacial periods on these time scales. Parts of the carbon cycle may even amplify the long-term temperature changes.

On very long time scales (millions to tens of millions of years), the movement of tectonic plates and changes in the rate at which carbon seeps from the Earth's interior may change the temperature on the Earth thermostat. Earth has undergone such a change over the last 65 million years, from the extremely warm climates of the Cretaceous (roughly 145–65.5 million years ago) to the glacial climates of the Pleistocene (roughly 1.8 million to 11,500 years ago; see the Geologic Time Scale in Appendix I).

At the ocean surface, where air meets water, carbon dioxide gas goes in and out of the ocean in a steady exchange with the atmosphere. Once in the ocean, carbon dioxide gas reacts with water molecules to release hydrogen, making the ocean more acidic. The hydrogen reacts with carbonate from rock weathering to produce bicarbonate ions. Many organisms living in ocean waters use calcium carbonate to build their shells and skeletons while others use silica and vertebrates use tricalcium phosphate to build bones and teeth.

9.5.1 Sources of Atmospheric Carbon Dioxide

The vast majority of atmospheric carbon dioxide is from the burning of fossil fuels by humans for heat and electricity, the internal combustion engine which uses a derivative of fossil fuel (gasoline), the making of cement, and the conversion of methane coming from shallow seas and the melting of permafrost, in addition to some of the sources listed above. Volcanoes also emit carbon dioxide to the atmosphere but in much fewer quantities than does humankind. The latter (humankind) emits over 100 times the amount of the former (volcanoes).

Sources of atmospheric CO_2 can be divided into natural and anthropogenic. Natural CO_2 includes that from animals, the ocean surface, and volcanoes.

Anthropogenic sources include the burning of fossil fuels (power stations and transportation), cement production, and land-use changes (principally deforestation).

Methane is converted to carbon dioxide in the atmosphere by a simple chemical reaction:

$$CH_4 + O_2 = CO_2 + H_4{}^{\wedge}$$

$$H_4 \text{ is a gas and is driven off.}$$

9.5.2 Oxidation – Reduction of Carbon

Carbon dioxide (CO_2) is a product of the oxidation of carbon. Methane (CH_4) is an example of reduction in the state of carbon. Pure carbon (C) exists by itself in nature in only two minerals, diamond and graphite. Graphite is what is used as “lead” in pencils which is not lead (Pb) at all.

Carbon occurs in nature in many different natural substances such as coal, oil, natural gas, and the minerals calcite, aragonite, and dolomite. Calcite and dolomite are major rock-forming minerals (limestone and dolostone, respectively) and aragonite occurs as “mother of pearl” on the inside of certain sea shells.

The majority of carbon is stored in the Earth in the form of carbonates. Carbonates cannot be used as fuel because the carbon is bound up in the rocks and is inaccessible. Other sources of carbon that can be used as fuel are coal, oil (petroleum), and natural gas.

9.5.3 Sinks of Atmospheric Carbon Dioxide

Carbon dioxide readily dissolves in water, and the oceans provide a huge reservoir of carbon. Across the World Ocean there is a continual cycle of equilibration of dissolved carbon dioxide in water with carbon dioxide in the atmosphere. According to the Second Law of Thermodynamics, if ocean water is cooler than the air above it, CO_2 will dissolve into the ocean along with the heat exchange and become a sink for the greenhouse gas. Where the air over the ocean is cooler than the water, ocean water will give up heat as well as CO_2 to the atmosphere and become a source of the greenhouse gas. The physics of the ocean-atmosphere exchange of CO_2 is not quite that simple because of the partial pressure of the gases in the two media.

The partial pressure of a gas is a measure of thermodynamic activity of the gas’s molecules. Gases will always flow from a region of higher partial pressure to one of lower pressure; the larger this difference, the faster the flow. Gases dissolve, diffuse, and react according to their partial pressures, and not according to their concentrations in gas mixtures or liquids.

Around 88,000 million tonnes of carbon is released from the surface of the world’s oceans each year, with an annual uptake by the oceans of 90,000 million tonnes. Consequently, the net uptake of carbon dioxide by oceans is estimated to be approximately 2,000 million tonnes annually.

Chemists and chemical oceanographers tell us that the carbon dioxide which dissolves in our oceans occurs in three main forms. Aside from the normal carbon dioxide form, it is also found as bicarbonate and carbonate ions. Most, about 90% exists as bicarbonate with carbonate ions acting as the link between carbon dioxide and bicarbonate. As concentrations of carbon dioxide increase, the supply of carbonate ions becomes limited and so the oceans become less and less able to take up carbon dioxide from the atmosphere.

The ocean currently acts as a sink for carbon dioxide. There is constant interchange between the ocean surface and the atmosphere. Photosynthesis by surface algae and diatoms provide a sink in addition to the interchange between ocean surface water and the atmosphere. Constant agitation by waves and ocean currents also cause CO_2 to escape the oceans.

The other major sinks of atmospheric CO_2 are sediments, soils, land vegetation and photosynthesis by land plants and ocean algae and diatoms.

9.5.4 *Carbon Cycle Disequilibrium*

If the amount of carbon emitted to the atmosphere equaled the amount of carbon being removed by sinks, the carbon cycle would be in equilibrium. But this is not the case and the carbon cycle is in disequilibrium primarily because more carbon is being released to the atmosphere than is being taken up by the carbon sinks. This excess carbon production in the atmosphere has been the case since the Industrial Revolution began and has been increasing since the beginning of fossil fuel burning. As a result of this loss of equilibrium, the Earth's temperature is rising.

It is assumed that prior to the Industrial Revolution the carbon fluxes into and out of the carbon cycle were equal. But after the Industrial Revolution began, more carbon has been emitted to the atmosphere and the CO_2 concentration in the atmosphere has dramatically increased. This disequilibrium has caused a perturbation in the climate system and the system is in the process of readjustment; this readjustment is resulting in the climate system warming.

As of June 30 of 2012, the carbon dioxide level in the atmosphere stood at 400 ppm as measured by the U.S. National Oceanic and Atmospheric Administration (NOAA). One year ago (in May of 2011), the CO_2 level stood at 393.06 ppm. The value 10 years ago on the above date was 373.93 ppm (see IPCC Emission Scenarios in Fig. 9.3).

If the current trend continues with the business-as-usual high emissions path, the consequences for the planet could be dire.

Some of the impacts listed in the IPCC 2007 AR4 report for global warming of 2–4.5°C above pre-industrial levels include:

- Hundreds of millions and possibly over a billion humans exposed to increased stress on water resources;
- 30–40% of species at risk of extinction around the globe;
- About 30% of global coastal wetlands lost. This may be much greater if the ice caps of Greenland and Antarctica collapse;
- Increased damage from floods and storms;
- Widespread coral reef mortality;
- Terrestrial and oceanic biospheres tend toward a net carbon source;
- Reduction in agricultural productions;
- Increased human morbidity and mortality from heat waves, floods, and droughts.

9.5.5 *Restoring Carbon Cycle Equilibrium*

Carbon dioxide stays in the atmosphere for hundreds or possibly as long as a thousand years. The atmosphere contains a reservoir of carbon dioxide which is being added to constantly as it has been since before the Industrial Revolution. If carbon dioxide could be reduced to the level that it was before humankind began adding it to the atmosphere and before the Industrial Revolution (~280 ppm), the system would return to a state of equilibrium if there was no future perturbation to the climate system. But the prospect of this happening during this century (the twenty-first) is not good. Even if all additions of CO_2 to the atmosphere stopped suddenly today there would still be warming for at least the next 30 years or so due to the residual CO_2 in the atmosphere.

It can be seen in Fig. 9.2 that by far the ocean is the largest reservoir of CO_2 on the planet. The solubility of carbon dioxide in ocean water is greater when the water is cold and less when it is warm. The solubility decreases as the ocean water warms and as the ocean warms it becomes a source of CO_2 rather than a sink. One of the dangers of global warming is that the oceans will begin to give up the tremendous amounts of stored CO_2 and this could happen rather suddenly. Climate change scientists know from geologic and ice core data that major climate changes have occurred rather suddenly in the past and this may have happened as a result of the ocean becoming a source of CO_2.

The release of CO_2 from ocean water is analogous to opening a warm carbonated soft drink. The ocean chemistry is more complex than that but the analogy is appropriate. Warm water gives up its CO_2 with release of pressure (opening the can or bottle, especially if shaken vigorously). This occurs in oceanic water when there is upwelling from the deep ocean, especially when one considers that the upwelling is from the cold deep water to the warmer oceanic surface water. Warmer water gives up CO_2 (a source) while colder water absorbs it (a sink).

The additional carbon dioxide in the atmosphere is causing additional warming. This is an example of a positive feedback loop. Carbon dioxide in the atmosphere causes the ocean to warm and the ocean gives up more carbon dioxide to the atmosphere which causes more warming, etc.

Restoring carbon dioxide equilibrium is not possible under the current circumstances of humankind's continuing to add an increasing amount of carbon dioxide and other greenhouse gases to the atmosphere as time passes. The disequilibrium in the carbon cycle will continue to grow and the planet will continue to warm as long as nothing changes in the disequilibrium equation. In order to stop or at least reduce the effects of global warming, atmospheric concentration of carbon dioxide must be reduced to 350 ppm or less, according to some of the world's leading scientists active in climate change science.

9.6 Methane (CH_4)

Methane (CH_4) is a greenhouse gas that remains in the atmosphere for approximately 9–15 years. It is approximately 25 times more effective in trapping heat in the atmosphere than carbon dioxide (CO_2) over a 100-year period and is emitted from a variety of natural and human-influenced sources. Human-influenced sources include landfills, natural gas extraction, animal flatulence, petroleum systems, agricultural activities especially the cultivation of rice, coal mining, stationary and mobile combustion, wastewater treatment, and certain industrial processes.

Methane is the primary constituent of natural gas and is an important energy source. As a result, efforts to utilize methane emissions can provide significant energy, economic and environmental benefits if precautions are made to prevent its escaping into the atmosphere and from exploding due to a spark.

9.6.1 Sources and Sinks of Atmospheric Methane

Methane is emitted to the atmosphere from both anthropogenic and natural sources. Human activities include the burning of fossil fuels, animal enteric fermentation, rice cultivation, biomass burning, and waste management. Natural sources of methane are wetlands, gas hydrates (methane clathrates) in ocean water, melting permafrost, termites releasing methane from woody tissue, the ocean, freshwater bodies, soils, coal, and wildfires. Accidental explosions related to the underground mining of coal are usually the result of explosions of methane gas.

Methane is a more powerful greenhouse gas than carbon dioxide, being about 25 times more effective in capturing and re-radiating infrared heat back to the Earth's surface.

Each greenhouse gas has a global warming potential (GWP) which is defined as follows: the GWP of a greenhouse gas is the ratio of heat trapped by one unit mass of the greenhouse gas to that of one unit mass of CO_2 over a specified time period. The global warming potential represents how much a given mass of a chemical contributes to global warming over a given time period compared to the same mass of carbon dioxide. Carbon dioxide's GWP is defined as 1.0.

As part of its scientific assessments of climate change, the Intergovernmental Panel on Climate Change (IPCC) has published reference values for GWPs of several greenhouse gases. While the most current estimates for GWPs are listed in the IPCC's Fourth Assessment Report, the U.S. EPA analyses use the 100-year GWPs listed in the IPCC's Second Assessment Report (SAR) to be consistent with the international standards under the United Nations Framework Convention on Climate Change (UNFCCC; IPCC 1996). According to the SAR, methane is 21 times more effective at trapping heat in the atmosphere when compared to CO_2 over a 100-year time period, so its GWP is 21.

Methane is more abundant in the Earth's atmosphere today than it has been in at least the last 400,000 years based on analyses of ice cores.

Methane in the atmosphere has increased as humans have continued to burn fossil fuels. Currently the amount of methane emitted to the atmosphere is greater than is being removed, so its concentration is increasing. The rate of growth of methane concentration in the atmosphere is comparable to that of carbon dioxide.

The greatest potential for massive releases of methane to the atmosphere is from methane clathrates in permafrost and shallow marine continental shelves, particularly in the Arctic. The shallow seas north of Canada and Siberia have already been seen to be releasing methane bubbles to the atmosphere. As these seas continue to warm, the release from these areas will become greater.

Scientists think that at least some of the major episodes of species extinctions in the geologic past have been as a result of relatively sudden methane releases, and this is a reason for concern. Is the Earth heading for another mass extinction? All we can conclude at present is that trends of temperature and bubbling methane releases are leading us in that direction.

Sudden releases of methane causing rapid global warming and feedbacks have been referred to as the "Clathrate Gun Hypothesis" and have been proposed as a cause of the relatively sudden onset of interglacial intervals during the Pleistocene.

The major sink for methane is the chemical reaction with hydroxyl radicals (OH-) in the atmosphere and the conversion to carbon dioxide. Other sinks of methane are stratospheric removal by hydroxyl radicals and consumption by microbial communities in the upper reaches of soils.

9.7 Nitrous Oxide

Nitrous oxide (N_2O) is a long-lived important greenhouse gas that is commonly known as "laughing gas" because of its use as an anesthetic in medical procedures. It has an atmospheric lifetime of 120 years and has a GWP of 310 over 100 years. It gives rise to nitric oxide (NO) when in contact with oxygen. At room temperature, nitrous oxide is colorless, non-flammable with a sweet smell and taste. It is used in rocketry and as a propellant in auto racing.

Nitric oxide reacts with ozone and is an ozone depleting substance (ODS).

9.7.1 Sources and Sinks of Atmospheric Nitrous Oxide

The primary sources of human-influenced emissions of nitrous oxide to the atmosphere are agricultural soil management, animal manure management, sewage treatment, mobile and stationary fuel combustion, adipic acid, and nitric acid production. Nitrous oxide is also emitted naturally from a wide variety of biological sources.

Tropical soils are probably the most important source of N_2O to the atmosphere and as the tropics expand toward higher latitudes with global warming, this is likely to increase. The ocean is also an important source of nitrous oxide, as are cultivated soils, biomass burning, and such industrial sources as nylon production.

The major sinks of N_2O are stratospheric photo-oxidation and photo-dissociation. Consumption by soils may be a small sink but this has not been quantified.

9.7.2 Increases in Atmospheric Nitrous Oxide Concentration

In 1998, the atmospheric concentration of nitrous oxide was 314 ppb, an increase of 44 ppb from its concentration in the pre-industrial level of 270 ppb.

9.8 Halocarbons

The halocarbons include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), methylhalides, carbon tetrachloride (CCl_4), and the halons (bromides). All of the halocarbons are strong greenhouse gases and remain in the atmosphere for several decades. Also, halocarbons that contain chlorine and bromine contribute to stratospheric ozone depletion. The chlorine and bromine halocarbons have largely been reduced in production due to the Montreal Protocol and its amendments.

9.8.1 Sources and Sinks of Halocarbons

The CFCs and HCFCs are totally anthropogenic and do not occur in nature. Their presence in the atmosphere is entirely artificial. They have been used extensively in foam production, as aerosol propellants, in air conditioning units, and refrigerants.

The Montreal Protocol has been effective in reducing atmospheric concentrations of CFCs and HCFCs and provides an example of the benefits of an international agreement, the terms of which have been adhered to and have resulted in avoiding a potential environmental crisis. Ozone depletion, if allowed to continue unabated, would result in increased risk of cancer, respiratory distress, and other health-related illnesses. The expanding ozone thinning in the Northern Hemisphere is currently a reason for concern.

Halocarbons are destroyed primarily by photo-dissociation and photo-oxidation in the stratosphere. They are relatively inert and remain in the atmosphere for long periods. Methylhalides and HCFCs are removed from the troposphere mainly by reactions with OH and NO_3. Some of these gases are removed from the atmosphere by the ocean.

9.8.2 Increases in Atmospheric Halocarbons Concentration

Concentrations of halocarbons in the atmosphere are measured in parts per trillion by volume (pptv). Concentrations greatly increased when production increased in the 1930s until the Montreal Protocol. There is indication that their concentration has decreased substantially since the protocol was implemented.

9.9 Ozone

Ozone (O_3) is found throughout the atmosphere but is a pollutant in the troposphere and beneficial in the stratosphere. There is concern at present about an Arctic ozone hole, but an ozone hole over the Antarctic has been measured since the 1950s as seen in Fig. 9.4.

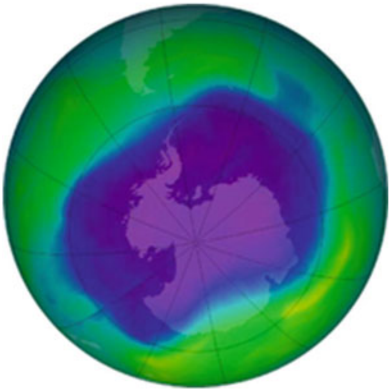

Fig. 9.4 View from the Earth's South Pole. Image of the largest Antarctic ozone hole ever recorded (September 2006, NASA, Public Domain)

Because the Earth is warming, temperatures in the troposphere warm while the stratosphere cools. The North Pole has experienced recent cold stratosphere temperatures and a reduction of ozone. Stratospheric ozone forms a blanket around the Earth about 12 miles up in the atmosphere and serves to protect life on Earth from harmful UV radiation from the Sun.

A continuing stratospheric cooling is reducing the ozone layer to about one half of its normal thickness. An ozone hole is not an actual hole, but a severe thinning of the polar ozone layer. Some scientists are predicting that the thinning could reach as far south as New York City during the twenty-first century.

The Arctic ozone hole could expose over 700 million people plus wildlife and plants to dangerous ultraviolet rays from the Sun. This seems to be the trend due to continued global warming and destruction of ozone in the stratosphere.

Global warming is depleting the ozone layer throughout its extent as the stratosphere cools. Stratospheric clouds form in the ozone layer and chemical reactions take place within them. These reactions activate chlorine ions present and make it easier for destruction of the ozone layer. The prediction is that within the next 20 years, the Arctic ozone hole will be as big if not bigger than the one currently over the South Pole. This Arctic ozone reduction could be blown south by high-altitude winds and could appear over much of the most heavily populated areas of North America and Europe. Scientists estimate that a 10% reduction in ozone will result in a 25% increase in non-melanoma skin cancer rates for temperate latitudes by the year 2050. A larger decrease in the ozone concentration could bring an epidemic of skin cancer and other maladies.

Scientists predict that if the Arctic ozone hole continues to expand, it will not recover as easily as had been thought. More polar clouds are forming in the stratosphere which activate stratospheric chlorine and they remove nitrogen compounds that act to moderate the destruction of ozone. The degree of Arctic ozone destruction in 2011 is unprecedented but it is not surprising and it will continue for some time into the future.

9.10 Other Trace Gases

The other trace gases like nitrogen oxides (e.g., NOx), carbon monoxide and the volatile organic compounds (VOCs) have little direct effect on greenhouse gas radiative forcing in the atmosphere. But they have indirect effects on other atmospheric chemicals such as ozone.

Nitric oxide (NO) is an air pollutant produced by coal-fired power plants and automobile exhausts. Nitric oxide in the atmosphere combines with water to form nitric acid, which is the main acid causing acid rain. It is also one of the chemicals that contribute to ozone depletion.

9.11 Atmospheric Residence Time of Greenhouse Gases

Each greenhouse gas has an atmospheric resident time, i.e., how quickly the gas is removed from the atmosphere. This resident time varies depending on several factors, such as its concentration, its inertness or reactivity, how soon it will be taken up by the ocean, microbes, or other aspects of the Earth systems. Carbon dioxide, the major greenhouse gas responsible for global warming, has an adjustment time of from 50 to 200 years. Methane has an adjustment time of from 12 to 17 years while for nitrous oxide it is 120 years. Lifetimes in the atmosphere for other greenhouse gases are quite variable.

All of the greenhouse gases with the exception of ozone and the CFCs have increased in atmospheric concentration in the last 260 plus years since the beginning of the Industrial Revolution.

Additional Readings

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