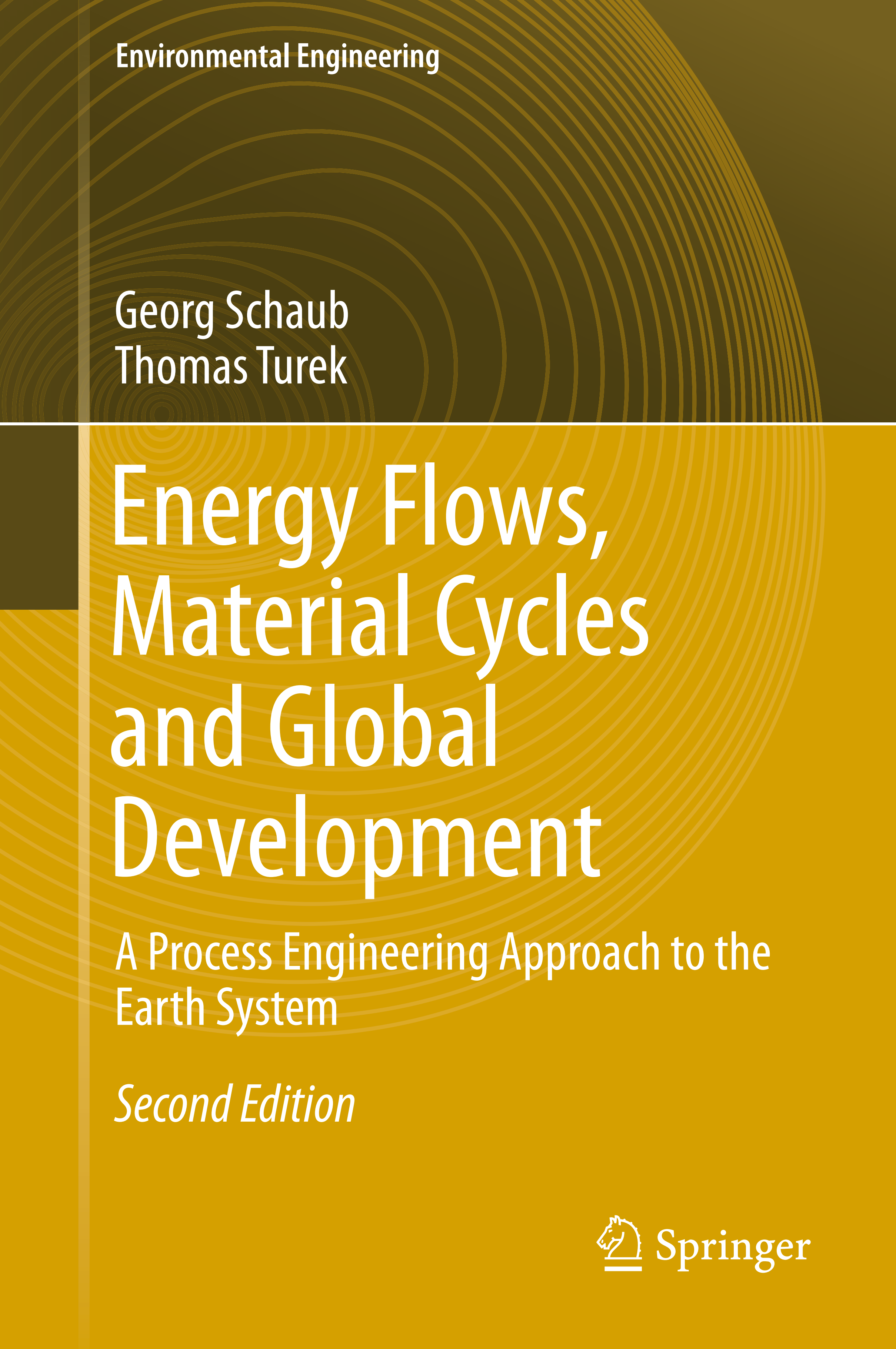

Environmental Engineering

Georg Schaub
Thomas Turek

Energy Flows, Material Cycles and Global Development

A Process Engineering Approach to the Earth System

Second Edition

Springer

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A Process Engineering Approach to the Earth System

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Preface

Why a Second Edition?

Since the first publication of our book (or since the end of our data compilation 2009) there have been important new developments: (i) significant increases in anthropogenic energy and material flows due to economic growth in significant parts of the world, (ii) changes in energy policy in some countries, in particular in Germany (*Energiewende*), as a result of the accident in the nuclear power plant in Fukushima, with goals defined and measures initiated for a future energy supply without nuclear and fossil sources, (iii) cheap sources for natural gas like shale gas created temptations to forget about energy saving.

In addition to these points we thought of addressing some new aspects that today we consider important enough to include in a new edition. Examples are resources of materials related to new energy technology (like lithium), resources important for feeding the growing world population (like phosphorus), as limitations for anthropogenic activities on Earth, or potentials for renewable energy sources.

Acknowledgments

When preparing the manuscript of the second edition, we had support from various sides. Again, Stefan Pinnow did the skillful processing of the manuscript using LaTeX, Marion Benoit helped by typewriting, and Amy Koch helped improve the text and make it more understandable to the general reader. Jörn Brauns prepared the new figures. We thank them all.

Karlsruhe — Georg Schaub
Clausthal-Zellerfeld — Thomas Turek
January 2016

Why a Process Engineering Approach to the Earth System?

Engineers involved in the handling, processing, and utilizing of materials and energy are constantly faced with the environmental and economic effects of their activities. These include environmental changes on local, regional, and global scales, as well as the depletion of resources and the search for new raw materials and energy sources. This has been the experience of the authors during their professional activities as chemical engineers in industrial research and development, and in academic research and teaching in various areas of fuel chemistry and reaction engineering.

This book is based on a course that has been held for engineering students for more than 10 years. In writing this book, the authors were motivated by the following questions:

a) What are the factors determining macroscopic material and energy flows in the Earth's biogeosphere? What is the appropriate approach to understand potential perturbations of natural cycles, caused by human activities and to assess significant anthropogenic terms?
b) When using materials and energy, are human societies today and for the foreseeable future limited by the depletion of resources or more so by global environmental changes? As an example, discovery of large usable gas hydrate resources as a fossil energy source, would it be fortunate or more like a curse?
c) Given the considerable technology innovation and research activities ongoing worldwide: how to deal with the obvious lack of synthesis and integration approach?
d) As for the industrialized countries, to what extent can they serve as examples for less-developed countries? What are appropriate technology options for sustainable development?

Our book is intended to give a basic understanding and orientation and to stimulate discussion of these questions. It addresses students in (chemical and biotechnological) process engineering, also in other fields and anyone interested, with a basic knowledge in natural sciences. It is supposed to stimulate discussions about science, technology, and policy aspects of global development. The authors think that *development* gives a better match with the engineering way of thinking than *global change*, as it reflects *solving problems* in addition to *analyzing problems*.

Acknowledgments

This book owes its existence to the course on Energy Flows, Material Cycles and Global Development taught at the Universität Karlsruhe (today Karlsruhe Institute of Technology, KIT). The course was initiated in 1990 by Lothar Riekert, and was

continued and extended first by TT and later by GS. We particularly want to thank Lothar Riekert, our academic teacher during the 1970s (GS) and the 1980s (TT), for his inspiration. We are also indebted to Hans-Günther Lintz and Kurt Hedden who introduced reaction engineering fundamentals and the view on process engineering systems to our thinking.

Many individuals in Karlsruhe and Clausthal-Zellerfeld, colleagues and students, inspired us with creative ideas or provided us with technical assistance. During the early stages of the course, there were, in particular, Dominik Unruh and Martin Rohde who shared with us the conceptual view of the Earth system and contributed ideas on how to present individual topics. Christine Minke expertly prepared most of the figures, and Stefan Pinnow did the skillful processing of the manuscript using LaTeX. Jens Riede and Kristian Voelskow carried out part of the mathematical simulations. Marion Benoit and Kyra Pabst contributed parts and pieces of the manuscript and the figures. Amy McDaniel Koch helped improve our foreign language skills and make the text more understandable to the general reader. We thank them all.

This book is dedicated to our wives whose assistance and patience helped us during the time period of thinking and writing, and to Tonio and Anna-Chiara who take a great interest in global development.

Karlsruhe
Clausthal-Zellerfeld
June 2010

Georg Schaub
Thomas Turek

Contents

Acronyms

ADP	Adenosine diphosphate
API	American Petroleum Institute
ATP	Adenosine triphosphate
BCE	Before the Common Era
BTL	Biomass-to-liquid
CAM	Crassulacean acid metabolism
CCS	Carbon capture and storage
CE	Combustion engine
CFC	Chlorofluorocarbon
CHP	Combined heat and power
CSP	Concentrating solar power
GCM	General climate model
DC	Direct current
DDT	Dichlorodiphenyltrichloroethane
DNA	Deoxyribonucleic acid
DU	Dobson unit
EUR	Estimated ultimate recovery
FAME	Fatty acid methyl esters
FAO	Food and Agriculture Organization
GAP	Good agricultural practice
GNI	Gross national income
GPCC	Global Precipitation Climatology Centre
GPP	Gross primary productivity
HDI	Human development index
HHV	Higher heating value
HVO	Hydrogenated vegetable oils
IEA	International energy agency
IPCC	Intergovernmental panel on climate change
IUGS	International Union of Geological Sciences
LHV	Lower heating value
LPG	Liquid petroleum gas

NASA	National Aeronautics and Space Administration
NPP	Net primary production
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
PEM	Polymer electrolyte membrane
PGM	Platinum group metals
POP	Persistent organic pollutant
PPFD	Photosynthetic photon flux density
PV	Photovoltaic
PVC	Polyvinyl chloride
RNA	Ribonucleic acid
RF	Radiative forcing
TGV	Train à Grande Vitesse
WCED	World Commission on Environment and Development

Chapter 1
Introduction and Fundamentals

This chapter discusses the relevance of environmental effects caused by humans and the concept of sustainable development. Many of these effects take place on a global scale. Thus they are relevant for the Earth system (Steffen et al. 2005) and presently constitute a major challenge for human societies. The second section deals with the definition of systems, their balances, and their properties with special emphasis on dynamic and feedback situations. In the third section, it is described how systems respond to internal processes and to changes of their surroundings. Classical thermodynamics distinguishes between different kinds of energies that can be interconverted without altering the sum of all energies. However, different kinds of energy have not the same quality and low-level energy cannot be completely transformed to higher levels. Second-law analyses using the concepts of entropy and exergy are required to describe the efficiency of these transformations. Finally, non-equilibrium thermodynamics devoted to real systems far away from equilibrium, where fluctuations and instability are of great importance, are briefly discussed.

1.1 The Starting Point: Sustainability and Global Change

During the Earth's history there have been profound changes in the chemical milieu at the surface, caused, for example, by the appearance of photosynthetic organisms. These changes, however, have occurred relatively slowly, with sufficient time for evolutionary change to keep pace (Schlesinger 1997). With the advent of industrialization and an increasing human population, environmental changes have occurred much faster, caused by human activities utilizing natural resources, concentrated forms of energy, or chemical materials produced for special purposes. Humans are utilizing large fractions of the resources that support all kinds of life on the planet Earth. Atmospheric gas concentrations of CO_2, CH_4, and N_2O, which had been stable for tens of thousands of years, are now increasing at rates of up to 1 % per year.

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Measurable changes of temperature and precipitation frequency have made people think about the complex relationships between human activities and environmental effects and have therefore become aware of their responsibility.

Scales of Environmental Effects

Environmental effects can be classified according to characteristic scales in time and distance. If a polluting species is emitted, e.g. as a gas into the atmosphere, it is transported by the natural convective transport mechanisms therein. The distance it can travel is determined by the rate of chemical decay, e.g. by photo-induced reactions, or also by removal, e.g. by absorption in precipitating rain or in surface ocean waters.

Sulfur dioxide (SO_2), if emitted for example from a combustion plant, has an average residence time of about 2 days in the atmosphere before it is absorbed in precipitating rain. During this time, it can travel with an assumed average wind speed of $10\,\mathrm{m\,s^{-1}}$ as far as 1700 km and may cause damage to the environment. When compared to the Earth's perimeter of about 40 000 km, this can be seen as a regional effect (see Fig. 1.1). During the 1960 s and 1970s, acid rain originating from SO_2 dissolved in rainwater could be observed in Scandinavia causing increased pH values in remote mountain lakes, although the sources of SO_2 were far away in central Western Europe or Great Britain. As a consequence, off-gas cleaning technology was developed and successfully applied, and atmospheric SO_2 concentra-

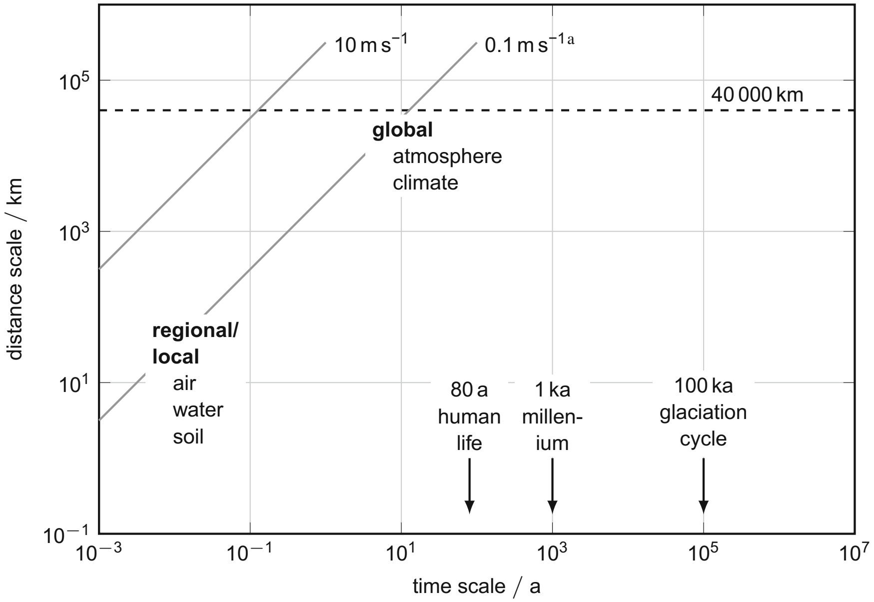


Fig. 1.1 Characteristic time and distance scales of environmental effects on Earth (examples: see text), after Graßl (1993), ^{a}velocities of horizontal transport in atmosphere ($10\,\mathrm{m\,s^{-1}}$) and in surface ocean ($0.1\,\mathrm{m\,s^{-1}}$)

tions decreased. This environmental problem could be solved. Other examples of regional/local effects are due to emitted particles, dust, or smoke that together with low wind speeds have led to critical immission conditions (*smog*) in large cities (like London, Mexico City) until smokeless fuels and off-gas cleaning were applied.

Atmospheric gas species with a longer residence time can travel with the winds longer distances than the Earth's perimeter. As a consequence, concentrations will be about the same at any location, independent of the location where the emission occurred. Examples are (i) the chlorofluorocarbons used in a variety of products, which have detrimental effects on the stratospheric ozone layer over the South Pole, and (ii) carbon dioxide as a product from burning coal and other fossil fuels, which reduces the amount of organic carbon stored underground and instead releases carbon as CO_2 into the relatively small reservoir of the atmosphere. The resulting increase of CO_2 concentrations are considered to enforce the greenhouse effect thus contributing to a temperature rise on Earth.

Today, the global environmental effects are seen as a major challenge for human societies. The example of chlorofluorocarbons has come close to a solution in the past 30 years by negotiating international agreements that limit and ultimately prohibit the production of the most critical species (see discussion in Sect. 4.7). In the case of CO_2, the challenge of slowing down concentration increases by drastically reducing fossil CO_2 emissions is both urgent and very difficult at the same time. It is difficult because investments for changing the present energy system to non-fossil energy sources are high, and severe disparities of economic development and prosperity among the nations make agreements challenging.

Concept of Sustainability and Global Change

Growing interest in considering interactions and potential conflicts helped the concept of sustainability to emerge as an overarching goal of development. It was adopted by UN agencies, by the Agenda 21 nations, and by many local governments and private-sector actors. The term sustainable development was defined by the World Commission on Environment and Development as *development that meets the needs of the present without compromising the ability of future generations to meet their own needs* (WCED 1987; IPCC 2007). The concept aims at a comprehensive and integrated approach to economic, social and environmental processes.

This book addresses important aspects of global development and their complex interactions from an energy and material flow view. Natural and anthropogenic flows are treated with particular emphasis on material cycles of individual chemical elements, such as the carbon cycle, with fossil CO_2 emissions as the most important anthropogenic flow. Principles of chemistry and thermodynamics as natural sciences are applied and directions for sustainable technology development are presented. Processes on Earth are treated as viewed through a *macroscope* (Figs. 1.2 and 1.3). It is well recognized by the authors that local/regional environmental problems are still among the most urgent to be solved in many locations on Earth. However global effects presently appear, from a systematic view, more complex and difficult to solve, both in terms of technological and political solutions.

Fig. 1.2 Satellite-based image of the entire Earth (http://visibleearth.nasa.gov)

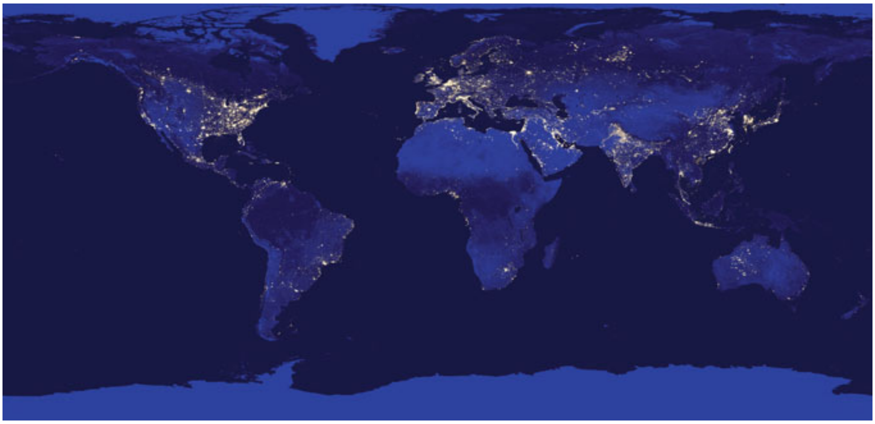


Fig. 1.3 Image of Earth's city lights based on NASA satellite data (http://visibleearth.nasa.gov)

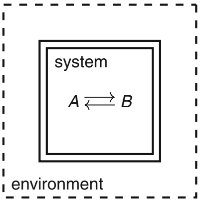
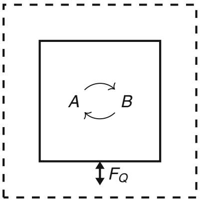
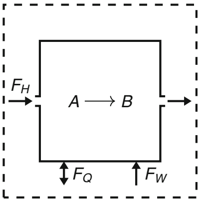
1.2 Systems and Balances

This section deals with the definition of systems and their balances. A system is in contact with its surroundings and may exchange flows of energy, materials, or other quantities. Inside the system, the considered quantities can be subject to change by source or sink terms. Complex systems with a spatial distribution of properties must be subdivided into appropriate control volumes for mathematical treatment. The behavior of any system can be calculated in the same way independent of the quantities or properties considered. While some systems remain in a time-independent state, in many cases dynamic changes must be taken into account. If systems are interconnected and influence each other, their dynamics are strongly coupled and lead to nonlinear and often unexpected feedback behavior. Systems that exchange flows over their boundary are sometimes capable of maintaining different states at exactly the same conditions depending on their history. A few selected examples will be presented to elucidate some important properties of dynamic systems.

1.2.1 Types of Systems and General Balances

One can distinguish between different kinds of systems, the most important characteristics of which are summarized in Table 1.1. Any system is defined by its content that is confined by a boundary and enclosed in an environment.

Table 1.1 Types of systems and their properties

Systems	Isolated	Closed	Open
			
Exchange of energy	No	Yes	Yes
Exchange of matter	No	No	Yes
Chemical transformation	No (equilibrium)	Yes (material cycles)	Yes
Examples	Dewar flask, universe (?)	Cooking pot, Earth	Human being, chemical reactor, atmosphere

An *isolated* system has no exchange of energy or matter over the system boundary. Consequently, any changes in composition or properties of the matter inside this system must cease – at least some time after the system was isolated from the surrounding environment – and the equilibrium state of the system will be eventually attained. A perfectly isolated system is an idealization of the reality, where it is difficult to prevent any exchange of energy or matter over a system boundary completely. A well-known example for an approximation of an isolated system is a Dewar flask. Such a container has an efficient insulation through a vacuum jacket and allows for the storage of materials such as liquefied nitrogen. Another example of an isolated system could be the universe, although little is known about the boundary of the universe and its possible surroundings. If the universe is an isolated system, after a very long time span it will reach the state of *heat death*, where all stars have burnt out and the complete universe is in thermal equilibrium.

A *closed* system is in contact with the environment through exchange of energy. A typical example is a cooking pot in which food is prepared at elevated temperatures. Chemical reactors are often operated as closed systems. After initial filling of the apparatus with the reacting components, the reactor contents are brought to the desired temperature and pressure. During the reaction, heat may be supplied or removed to maintain a certain temperature. After completion of the reaction, the products are cooled down and the procedure can be repeated. The Earth as a whole can also be considered to be a closed system as there is only very little exchange of material with the outer space. However, it receives an energy flow from the Sun that allows the Earth to maintain favorable temperatures for the biosphere (see Chap. 3). Many chemical transformations take place in an extended and complex system like the Earth. However, these conversions must proceed in cycles as will be discussed in detail in Chap. 4.

An *open* system exchanges not only energy, but also matter with its surroundings. Any living organism can be regarded as such a system as it is dependent on a continuous supply of food while it produces flows of waste and sometimes also heat. Chemical reactors are often used in such a flow-through configuration since it allows for the permanent supply of a product stream without the time and effort required during the intermittent operation of a closed system. Subsystems of the Earth are also open systems, e.g. the atmosphere that exchanges matter with the ocean, the land, and the biota therein.

The general form of balancing an open system is described in Table 1.2. Here, z is a quantity of the system such as mass or amount of a substance, energy, or the number of individuals in biological systems. The change of this quantity with time (*accumulation*) is caused by the sum of the exchanging flows over the system boundary as well as by sources or sinks inside the system. If the accumulation term is zero, the open system is at *steady state* and the considered quantity is independent of time. However, if flows over the system boundary and production terms are not in balance, the quantity z changes with time. An example for such a dynamic system behavior can be seen, if the number of individuals in a given country changes with time if a difference between death and birth rate is not compensated by immigration or emigration.

Table 1.2 System balances and typical examples

General form	Accumulation	= Sum of flows over system boundary	+ Production[a]
Mathematical form	$\frac{dz}{dt}$	$= \sum F_i$	$+F_p$
Examples	– Mass – Amount of substance – Energy – Number of individuals	– Mass flux – Heat flux – Radiation – Movements of population	– Chemical or biochemical transformation – Phase transition – Birth and death rate

[a] Source or sink

1.2.2 Example: Historical Development of Atmospheric CO_2 Concentration

The first example describing the behavior of dynamic systems is the development of the atmospheric carbon dioxide concentration during Earth's history. Figure 1.4 shows the development of the conditions on Earth from the very beginning until today. Although the Sun's luminosity was significantly lower in earlier times according to standard stellar evolution models, it is most likely that temperatures were higher than today in the early history of the Earth, perhaps by more than 50 K (Kasting 1993). The generally accepted explanation for this *faint young Sun paradox* is the presence of very high atmospheric concentrations of greenhouse gases (see Sect. 3.2), namely CO_2. In contrast, the oxygen content of the early Earth atmosphere was extremely low. Several physico-chemical, and later also biological, phenomena lead to a gradual change of the atmospheric composition until today's values of oxygen and carbon dioxide concentrations were reached.

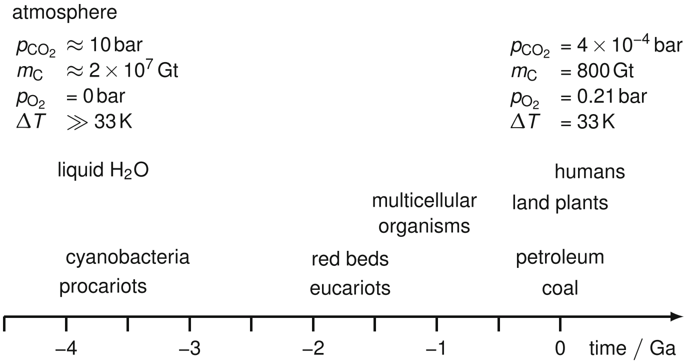


Fig. 1.4 Earth history with selected stations as well as initial and present atmosphere, rounded values, ΔT: temperature increase due to greenhouse effect (see Sect. 3.2)

To describe the time-dependent behavior of the atmospheric CO_2 concentration, we define the whole, well-mixed atmosphere as an open system and consider the flows over the system boundary (Fig. 1.5). The production term (see Equation in Table 1.2) can be neglected as carbon dioxide does not undergo chemical transformations in the atmosphere.

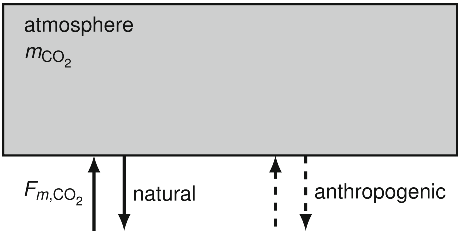


Fig. 1.5 Earth atmosphere as control volume for carbon dioxide

There are a variety of processes causing flows of carbon dioxide from and to the atmosphere that are summarized in Table 1.3. While volcanoes permanently transport CO_2 from the inner Earth to the atmosphere, absorption in the ocean and carbonate formation in rocks (*weathering*) are physico-chemical processes that remove carbon dioxide. Photosynthesis is another process that decreased the CO_2 concentration over long periods of time. Recently, fossil fuel combustion became an additional source of carbon dioxide. This process causes such an abrupt concentration rise at present that removal from large CO_2 point sources and subsequent storage (*sequestration*) is under discussion.

Table 1.3 Natural and anthropogenic flows of carbon dioxide from and to the atmosphere

	To atmosphere	From atmosphere
Natural	Volcanism	Carbonate formation
	Desorption from surface ocean	Absorption in ocean
	Respiration	Photosynthesis
	Biomass oxidation	
Anthropogenic	Fossil fuel combustion	(Sequestration?)

An explanation for the massive reduction of the atmospheric carbon dioxide concentration during the earlier Earth history is that the physico-chemical flow rates removing CO_2 were much higher than the release by volcanoes. Moreover, photosynthesis initially lead to a further large flow from the atmosphere to living and dead organic matter until it later became more or less balanced by respiration and biomass oxidation. Figure 1.6 summarizes the most important control volumes and flow rates to be considered.

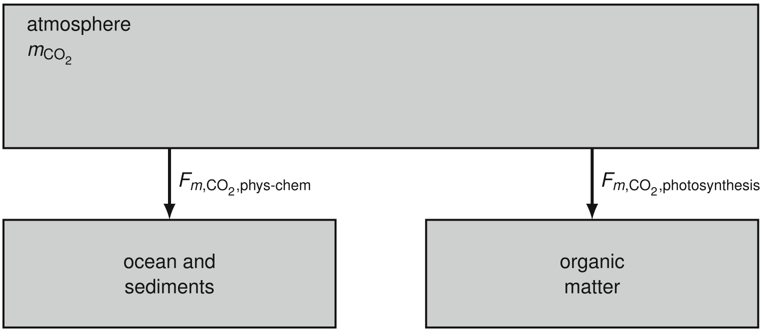


Fig. 1.6 Schematic of atmosphere and net fluxes caused by photosynthesis and physico-chemical phenomena (absorption, carbonate formation) during the earlier Earth history

If one summarizes all physico-chemical flows, the following balance for the development of the CO_2 mass in the atmosphere as a function of time is obtained (Eq. (1.1)).

$$\begin{aligned}\frac{\mathrm{d}m_{CO_2}}{\mathrm{d}t} &= \sum_{\text{in}} F_{m,CO_2} - \sum_{\text{out}} F_{m,CO_2} \\ &= -F_{m,CO_2,\text{phys-chem}} - F_{m,CO_2,\text{photosynthesis}}\end{aligned} \tag{1.1}$$

For the physico-chemical processes it is assumed that the flow rate from atmosphere to ocean and sediments is directly proportional to the actual CO_2 mass (Eq. (1.2)). This leads to an initially high but gradually diminishing removal rate of carbon dioxide. Photosynthesis evolved at time t_i and the corresponding flow rate is proportional to the carbon dioxide mass and also, as biomass builds up gradually, proportional to the time elapsed since the evolution of photosynthesis. This additional process strongly accelerates the CO_2 removal for a certain time until the biomass growth levels off at low carbon dioxide concentrations.

$$\begin{aligned} F_{m,CO_2,\text{phys-chem}} &= k_{\text{phys-chem}}\, m_{CO_2} & & \\ F_{m,CO_2,\text{photosynthesis}} &= 0 & \text{for} \quad & t \le t_i \\ F_{m,CO_2,\text{photosynthesis}} &= (t - t_i)\, k_{\text{photosynthesis}}\, m_{CO_2} & \text{for} \quad & t > t_i \end{aligned} \tag{1.2}$$

Figure 1.7 shows simulation results, expressed as atmospheric carbon dioxide partial pressure, obtained with the above described model and a comparison with climatically reasonable values. It can be seen that the model predictions are within the range of historical carbon dioxide partial pressures.

1.2.3 Characteristics of Dynamic Systems

The previous section has shown that the carbon dioxide content of Earth's atmosphere has changed dynamically throughout history. The same is true for many other para-

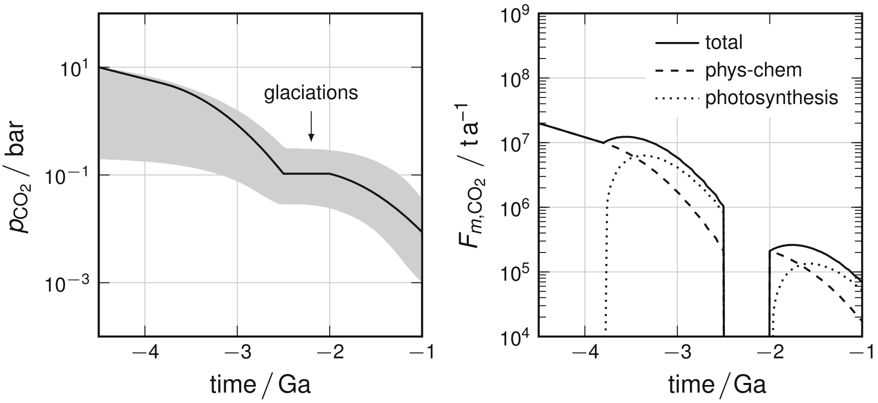


Fig. 1.7 Development of atmospheric CO_2 partial pressure during early history of the Earth, *left* comparison of data from Kasting (1993) with simulation results (parameters: $k_{\text{phys-chem}} = 1\,\text{Ga}^{-1}$, $k_{\text{photosynthesis}} = 3\,\text{Ga}^{-2}$, evolution of photosynthesis at $t_i = -3.8\,\text{Ga}$, no carbon flows during glaciation period between -2.5 and $-2.0\,\text{Ga}$, restart of biomass formation at $t_i = -2.0\,\text{Ga}$), *right* corresponding carbon dioxide flows

meters that are important for the biogeosphere, the development of which will be described in Sect. 2.2. In this section typical characteristics of dynamic systems will be discussed to provide some basic information necessary for understanding the complex behavior of the Earth system. As an example, the development of the yearly average global temperature since 1850 is depicted in Fig. 1.8. One can see that in the short term relatively large fluctuations of up to $0.3\,\text{K}\,\text{a}^{-1}$ occur. The average values over five years reveal that there was a period with relatively constant temperature

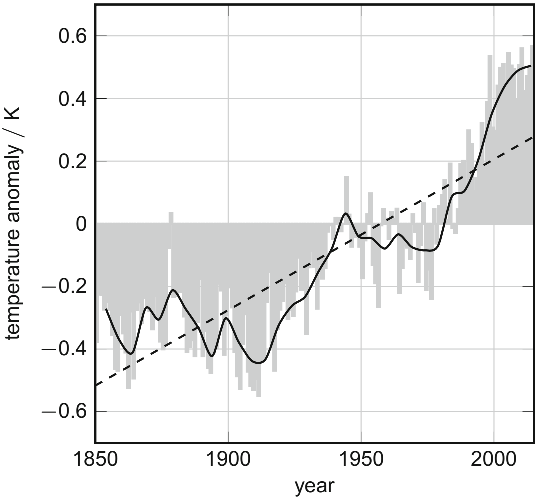


Fig. 1.8 Development of yearly average global temperature since 1850 (as anomaly from base period 1961–1990). Values calculated from land and sea surface temperatures (Brohan et al. 2006, updated with data until 2014 from the UK Met Office Hadley Centre, http://www.cru.uea.ac.uk/cru/data/temperature/), *solid line* average values over five years, *dashed line* linear trend

between 1850 and ca. 1920 and that the temperature has increased since then except for a period around 1940. Following the overall linear trend, the global temperature has risen by as much as 0.8 K during the last ca. 165 years. This typical feature of the complex Earth system is caused by the interaction of a great many individual effects in subsystems each having dynamic behavior.

Feedback Systems

If processes in different systems are interconnected and influence each other, their dynamics are strongly coupled and lead to nonlinear and sometimes unexpected behavior. This *feedback* situation is often encountered in engineering, biological systems, and the Earth system as a whole. To explain the basic phenomena in feedback systems, the carbon dioxide content of the atmosphere is again considered as an example. In contrast to the development during Earth's early history (see Fig. 1.7), the present situation is analyzed where the atmospheric carbon dioxide budget is additionally influenced by human activities (Fig. 1.9). For the following calculations of the future CO_2 concentration between 2000 and 2050 it was assumed that the atmosphere initially contained 2860 Gt carbon dioxide (780 Gt C) corresponding to a concentration of 370 ppm. The world population is supposed to increase linearly from 6×10^9 to 9×10^9 in 2050 while the per-capita carbon dioxide emission rate of $4\ \mathrm{t\ a^{-1}}$ is assumed to remain constant. In scenario (a) without feedback, the carbon dioxide flows caused by ocean and biomass uptake are set at constant values of 8 and $3.5\ \mathrm{Gt\ a^{-1}}$, respectively. These assumptions are in line with the fact that at present ca. 40 % of the anthropogenic carbon dioxide emissions are fixed in the ocean and the terrestrial biota (cf. Table 4.2). This scenario without feedback would lead to an increase from 370 to 490 ppm CO_2 in 2050 as shown in Fig. 1.10.

Many possibilities for deviations from this linear system behavior without feedback exist. *Positive* feedback with a resulting amplification of the rising carbon diox-

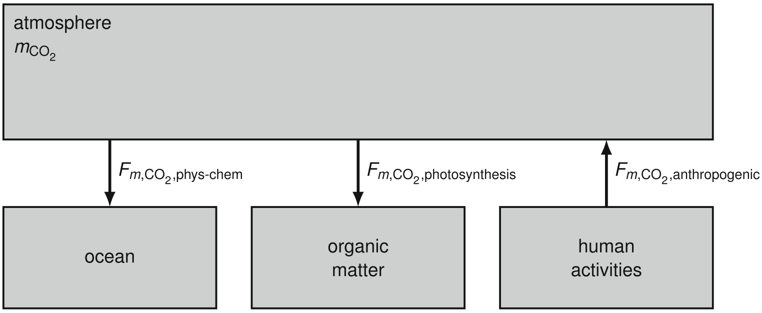


Fig. 1.9 Schematic of atmosphere and fluxes caused by anthropogenic carbon dioxide release, absorption in the ocean and photosynthesis

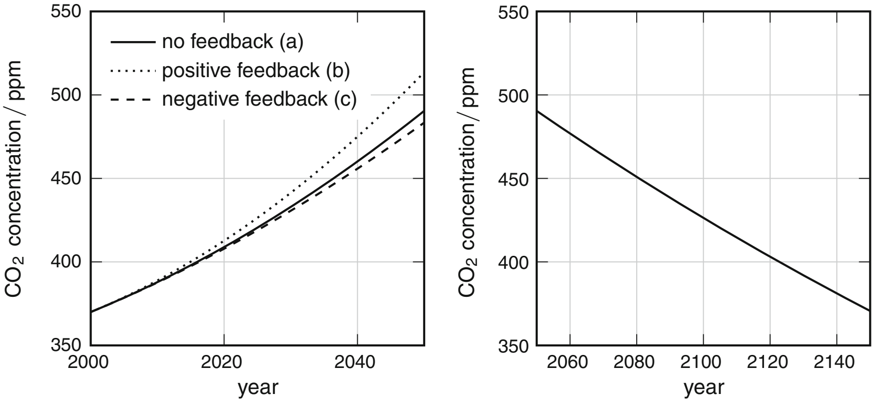


Fig. 1.10 Calculated future development of atmospheric CO_2 concentration, *left* results obtained between 2000 and 2050 for three different cases (see text), *right* decrease after 2050 for assumed termination of fossil CO_2 emissions

ide concentrations with time may be caused by a negative effect of the growing world population on the ability of the terrestrial biomass to act as a net CO_2 sink. Another positive feedback mechanism could be the decreased ocean uptake at rising water temperatures caused by lower carbon dioxide solubility. However both ocean uptake and biomass fixation of CO_2 might be enhanced by rising atmospheric concentrations leading to a *negative* feedback. For the mathematical calculation of a positive feedback scenario (b) it was assumed that the ocean uptake remains constant while the carbon dioxide fixation rate through photosynthesis linearly changes from $+3.5$ to -3.5 Gt a^{-1} in 2050 caused by the rising world population with intensified land use and deforestation. For this scenario, a significantly higher atmospheric concentration of 513 ppm is predicted for 2050. As an example for a negative feedback scenario (c) it was considered that the carbon dioxide flow to the ocean is proportional to the actual atmospheric concentration (see Eq. (1.2)) while the photosynthesis fixation rate was again set constant at 3.5 Gt a^{-1}. The simulation results depicted in the left diagram of Fig. 1.10 show that the more realistic consideration of the ocean uptake has only a minor stabilizing effect on the CO_2 concentration. However, if one assumes that anthropogenic CO_2 emissions and biomass uptake would be balanced from 2050 on, the calculated development of the carbon dioxide concentration shown in the right diagram of Fig. 1.10 reveals that the ocean is able to absorb large amounts of carbon dioxide over longer periods of time.

Another famous example for dynamic behavior of feedback systems is shown in Fig. 1.11 (left) where the number of furs from snow shoe hares and lynxes delivered to the Hudson Bay Company is depicted (MacLulich 1937). Drastic fluctuations for both species are observed and it appears that the maxima for the collected lynx furs follow the respective maxima for the hares with a phase shift of several years. The explanation for this oscillatory behavior is relatively simple. The predators (lynx) feed on prey (hares) and their population increases in phases with a sufficient number

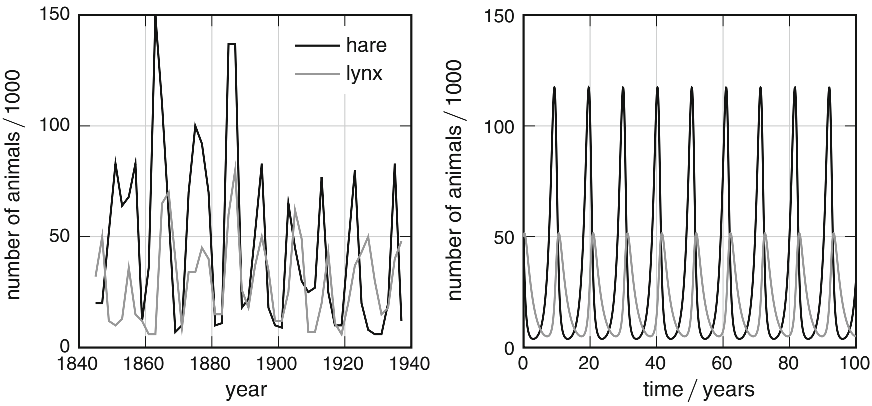


Fig. 1.11 Numbers of snow shoe hare and lynx according to data collected by the Hudson Bay Company (*left*, data from MacLulich 1937) and simulation results for simple mathematical model of oscillating predator–prey system (*right*), model parameters: $r_\text{H} = 1$, $r_\text{L} = 0.5$, $y_\text{HL} = 0.05$, $y_\text{LH} = 0.015$, initial values $N_{\text{H},0} = N_{\text{L},0} = 5 \times 10^4$

of prey. At the same time, however, the hare population decreases and the now much larger lynx population starts to drop as there is no sufficient food. Finally, the hare population is able to recover and the dynamic cycle starts again. In the 1920s Lotka and Volterra proposed independently a simple mathematical model to describe the population variations of the two species with time (Lotka 1925; Volterra 1926). It consists of two coupled nonlinear ordinary differential equations describing the number of hare N_H and lynx N_L (Eqs. (1.3) and (1.4)).

$$\frac{\text{d}N_\text{H}}{\text{d}t} = +r_\text{H}\, N_\text{H} - y_\text{HL}\, N_\text{H}\, N_\text{L} \tag{1.3}$$

$$\frac{\text{d}N_\text{L}}{\text{d}t} = -r_\text{L}\, N_\text{L} + y_\text{LH}\, N_\text{H}\, N_\text{L} \tag{1.4}$$

Here, r_H and r_L are the birth rate of hare and the natural death rate of lynx, respectively, while y_HL and y_LH describe the decrease of hare and rise of lynx populations caused by predator–prey interaction. The simulation results shown in the right hand side of Fig. 1.11 reveal that the model is capable of describing the most important features of the naturally observed population dynamics although it is oversimplified assuming unlimited growth of both species in the absence of any interaction.

Bossel (2004) has analyzed the behavior of a similarly simple coupled dynamic system represented by the two differential Eqs. (1.5) and (1.6). If parameter d has a value of -1, the coupled system exhibits stable behavior with damped oscillations (Fig. 1.12, left) while for $d = 0.6$ it becomes unstable with increasingly larger oscillations as a function of time. Many physical or electronic systems are capable of such dynamic performance. While damped oscillations may occur after initial excitation of an oscillating system due to loss of energy, forced systems may store the

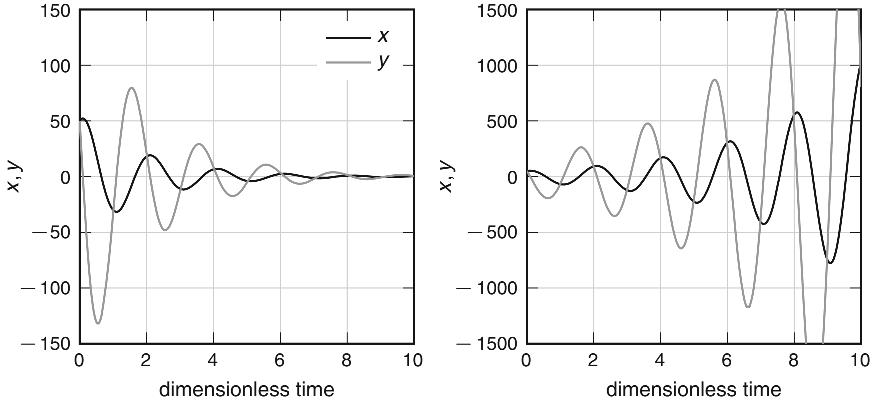


Fig. 1.12 Examples for stable and unstable behavior in a coupled system, parameters: $x_0 = y_0 = 50$, $a = 0$, $b = 1$, $c = -10$, stable behavior: $d = -1$, unstable behavior: $d = 0.6$

energy if excited at the resonance frequency causing increasingly stronger oscillations until the system is eventually destroyed.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = a\,x + b\,y \tag{1.5}$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = c\,x + d\,y \tag{1.6}$$

Systems with Multiple Steady States

Open systems far from equilibrium are able to maintain in different steady states although the processes in the system and the boundary conditions are the same. A well-known example for such behavior in reaction engineering is a continuously operated stirred tank reactor with heat exchange to a heat transfer medium (Fig. 1.13).

In the reactor, assumed to be perfectly mixed, a chemical reaction occurs the rate of which can be described as a function of reactant concentration c and temperature T with Eq. (1.7), where k_0 is the frequency factor and E_A is the activation energy.

$$r = k_0\,\mathrm{e}^{-\frac{E_\mathrm{A}/R}{T}}\,c \tag{1.7}$$

The average hydrodynamic residence time of the reactants with a volume flow rate F_V inside the reactor with a volume V can be calculated with Eq. (1.8).

$$\tau = \frac{V}{F_V} \tag{1.8}$$

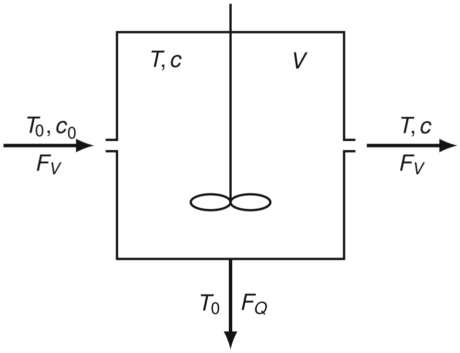


Fig. 1.13 Example of an open system with heat transfer to the surroundings: Continuously stirred tank reactor with cooling

The fractional conversion X in the reactor (Eq. (1.9)) can be obtained with the mass balance (Eq. (1.10)).

$$X = \frac{c_0 - c}{c_0} \tag{1.9}$$

$$X = \frac{\tau k_0 \, \mathrm{e}^{-\frac{E_A/R}{T}}}{1 + \tau k_0 \, \mathrm{e}^{-\frac{E_A/R}{T}}} \tag{1.10}$$

The temperature in the reactor T is influenced by the release of energy from the exothermic reaction, heat transfer through cooling, and the temperature of the flow at the reactor inlet. If we assume that the inlet temperature T_0 and the temperature of the heat transfer medium are equal, the following energy balance is obtained (Eq. (1.11)).

$$(T - T_0)(1 + St) = \Delta T_{\mathrm{ad}} \, X \tag{1.11}$$

Here, the Stanton number St (Eq. (1.12)) is a dimensionless group describing the cooling efficiency of the reactor with the heat transfer coefficient k_Q, the heat transfer area A_Q, the molar density ρ, and the molar heat capacity c_p of the reaction mixture. The adiabatic temperature rise ΔT_{ad} (Eq. (1.13)) is the maximum reactor temperature at complete conversion without any cooling and can be obtained with the reaction enthalpy $\Delta_{\mathrm{R}} H$ (see Sect. 1.3.1).

$$St = \frac{k_Q \, A_Q}{F_V \, \rho \, c_p} \tag{1.12}$$

$$\Delta T_{\mathrm{ad}} = \frac{(-\Delta_{\mathrm{R}} H) \, c_0}{\rho \, c_p} \tag{1.13}$$

The diagram on the left hand side of Fig. 1.14 depicts the conversion as a function of reactor temperature as obtained from the mass balance (Eq. (1.10), s-shaped curve) and the energy balance (Eq. (1.11), straight line). It can be seen that three steady-state solutions are mathematically possible for the chosen temperature T_0 of 280 K

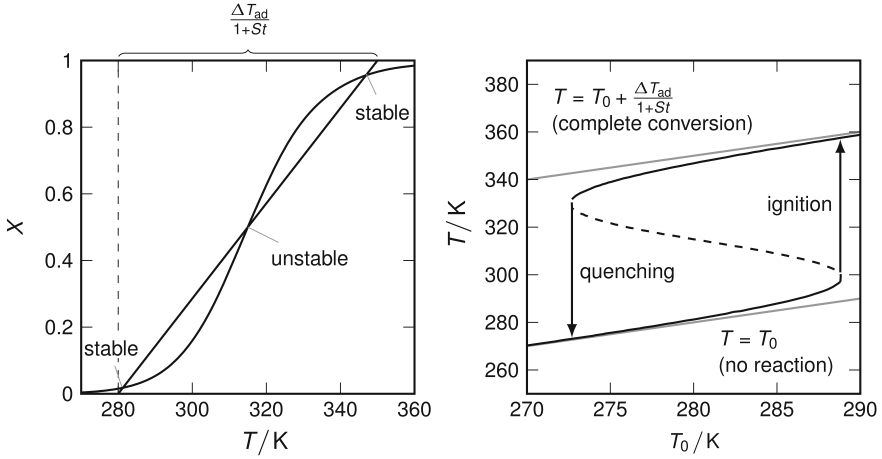


Fig. 1.14 Conversion of reactant as a function of reactor temperature in a cooled, continuously stirred tank with three steady-state solutions of the coupled heat and energy balances *left*, steady-state reactor temperatures for changing inlet and cooling medium temperatures *right*, parameters similar to the example given by Steinbach (1999): $\tau k_0 = 3 \times 10^{14}$, $E_A/R = 10\,500\,\mathrm{K}$, $St = 1.5$, $\Delta T_{ad} = 175\,\mathrm{K}$

and the parameters summarized in the caption of Fig. 1.14. The upper and lower solutions are stable steady states that can be realized in chemical reactors while the intermediate value is only an unstable mathematical solution of the coupled balances as will be shown later.

If the system has arrived in one of the two stable steady states, it will remain there as long as the conditions are not changed. The question of which of the two possible states is attained can only be answered if the history of the system is also considered. To illustrate this fact, the possible steady-state solutions of conversion and reactor temperature were calculated as a function of the inlet and cooling temperature T_0. The straight lines in the right hand side diagram of Fig. 1.14 are limiting cases where no reaction at all or complete conversion of the incoming reactants occur. At low values of T_0, there is only one steady-state solution of the coupled mass and energy balances and the system operates at low reactor temperature and corresponding conversion. During the increase of T_0, the reactor temperature moves along the lower solid line until, at around $T_0 = 288\,\mathrm{K}$, a sharp temperature increase occurs. The system ignites at this point and reaches a state with high conversion and temperature. If the temperature T_0 is now moved back to lower values, the system remains in the upper stable steady state until quenching of the system occurs at around $T_0 = 273\,\mathrm{K}$. It is obvious that the instable solutions (dashed line) between the quenching and ignition temperatures are only mathematical solutions that cannot be reached in real systems. This example from chemical reaction engineering illustrates how systems far from equilibrium may exhibit two (ore more) steady states depending on their previous history. It will be shown later that the Earth system as a whole may also attain multiple steady states under certain conditions (Sect. 3.5.1).

1.3 Thermodynamics: The Different Forms of Energy

Thermodynamics describes how systems respond energetically to processes in them and the changes of their surroundings. It distinguishes between different kinds of energies that can be interconverted without altering the sum of all energies. This first law of thermodynamics is easily comprehensible. However, the different kinds of energy do not have the same quality and energy with lower quality (e.g. thermal energy) cannot be completely transformed to a higher level (e.g. work) no matter how gradual and careful the conversion is carried out. This observation lead to the introduction of the concept of *entropy* as a measure for the irreversibility during energy transformation. Any real system that goes through a cycle of operations and returns to its initial state must lead to an increase of the entropy of the surroundings. Thus, as Kondepudi and Prigogine (1998) have pointed out, the increase of entropy distinguishes the future from the past: there exists an arrow of time. With the aid of entropy, one can also determine the *exergy* of a system, that is the maximum amount of work that can be obtained from matter in contact with its environment. While classical thermodynamics is limited to equilibrium states, more recent developments of non-equilibrium thermodynamics are devoted to real systems far away from equilibrium, where fluctuations and instability are of great importance. Surprisingly, it can be shown that entropy and irreversibility which destroy order near equilibrium can create order in systems far from equilibrium (Kondepudi and Prigogine 1998).

1.3.1 The First Law of Thermodynamics

The first law of thermodynamics states that the sum of all energies in a system remains constant. Energy cannot be destroyed or created, thus a perpetual motion machine of the *first kind* producing energy from nothing is not possible. Energy can have several different forms such as mechanical, chemical, thermal, and electrical energy. If a closed system (Fig. 1.15, left) at constant pressure without exchange of heat Q over the system boundary (an *adiabatic* system) is considered, any mechanical work W_{mech} or electrical energy W_{el} applied to the system will lead to an increase of its temperature (Eq. (1.14)).

$$F_{W,\text{mech}}\, t + F_{W,\text{el}}\, t = c_p\, n\, \Delta T \tag{1.14}$$

Here F_i is the energy flow per unit time t, c_p the molar heat capacity and n the total amount of substance in the system. If the same closed system would be operated at constant temperature in steady state, the energy conservation principle requires that the sum of the mechanical and electric power must be compensated by an equally high heat flow F_Q to the surroundings (Eq. (1.15)).

$$F_{W,\text{mech}} + F_{W,\text{el}} + F_Q = 0 \tag{1.15}$$

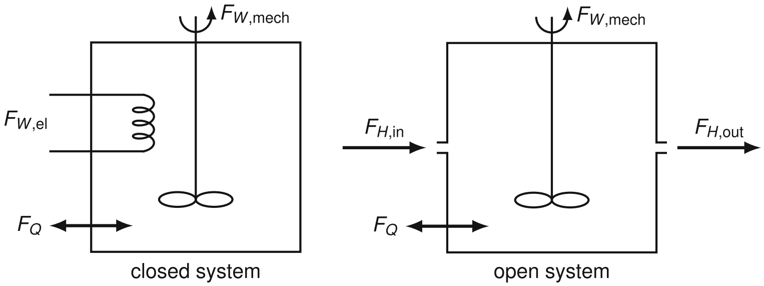


Fig. 1.15 Closed system *left* and open system *right* with different energy forms: electrical energy, mechanical energy, heat, enthalpy

In addition to these forms of energy, matter also contains chemically stored energy that in systems with constant pressure can be described by the enthalpy H. The energy balance for an open system with incoming and outgoing flows under steady-state conditions (Fig. 1.15, right) yields,

$$F_{W,\text{mech}} + F_Q + \sum_{\text{in}} F_{n,i} H_i - \sum_{\text{out}} F_{n,i} H_i = 0 \tag{1.16}$$

with H_i the molar enthalpy in J mol^{-1} of a component i entering or leaving the system with molar flows $F_{n,i}$.

Matter is able to store and release energy in several different ways. Enthalpy changes occur if the temperature in a system changes, during phase changes (e.g. melting/freezing or evaporation/condensation), and in case of chemical reactions. Chemical transformations are accompanied by an enthalpy change $\Delta_\text{R} H$ (Eq. (1.17))

$$\Delta_\text{R} H = \sum_i \nu_i \, \Delta_\text{f} H_i \tag{1.17}$$

where ν_i is the stoichiometric coefficient and $\Delta_\text{f} H_i$ the enthalpy of formation of component i. Reactions during which thermal energy is released have a negative reaction enthalpy and are called *exothermic*. The most important chemicals of present industrial economies are carbon and hydrogen containing fuels that are utilized via combustion processes forming carbon dioxide and water as reaction products. In the case where water is present in gaseous form, the negative reaction enthalpy of the combustion reaction is called the *lower heating value* (*LHV*) of the fuel. If water is liquid after combustion, the corresponding (negative) reaction heat is denoted as the *higher heating value* (*HHV*), the difference between *HHV* and *LHV* being the condensation enthalpy of water.

The first law of thermodynamics, however, does not state how efficient the conversion of one form of energy to another form may be. While it is easy to completely transform mechanical or electrical energy to thermal energy, the opposite way is much less facile and always accompanied by losses. If we consider the extreme case of an automobile in idling mode producing essentially thermal energy at ambient temperature, one can show that the energy chemically stored in the fuel is completely dissipated to the environment and cannot be regained.

1.3.2 The Second Law of Thermodynamics

Heat engines employing heat flows caused by temperature differences to perform mechanical work are still the backbone of industrialized societies. Examples are thermal power plants where fuels are combusted to produce high-temperature steam that performs mechanical work used to supply electrical energy, or automobiles. Carnot carried out a general analysis of such energy conversion systems and recognized that the amount of thermal energy transformed to mechanical work is limited and determined by the temperature difference during heat transfer from the hot (T_1) to the cold (T_2) reservoir. Independent of the properties of the engine and the nature of the cyclic process, there is an upper limit for the efficiency η of transforming thermal energy to work (Eq. (1.18)). If we assume that the colder reservoir is at ambient temperature (298 K) one can calculate that the maximum efficiency of a process with $T_2 = 1000\,\mathrm{K}$ is $\eta = 70\,\%$ while the use of boiling water at 373 K could retrieve only 20 % of the original energy content as useful work.

$$\eta = 1 - \frac{T_2}{T_1} \tag{1.18}$$

One formulation out of many existing variants of the second law of thermodynamics is that no engine working in a complete cycle and converting *all* the heat it absorbs into mechanical work exists. Note that such a perpetual motion machine of the *second kind* would not violate the energy conservation principle of the first law of thermodynamics. This finding lead to the definition of the thermodynamic quantity entropy S (Eq. (1.19)):

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T}. \tag{1.19}$$

While a theoretical *reversible* cyclic process would not cause a change in the system's entropy, one can show that any real *irreversible* cyclic process during which additional losses occur must lead to an increase of the entropy of the surroundings by output of additional heat.

With the aid of the entropy one can now quantitatively determine how much useful (mechanical or electrical) work a system can provide. This quantity is called *exergy*, the maximum amount of work that can be obtained from matter in contact with its environment. Exergy or second-law analysis has become an invaluable tool to identify the locations of energy degradation in a process and can lead to improved operation and technology (Rosen 1999; Dincer and Rosen 2007). To explain the

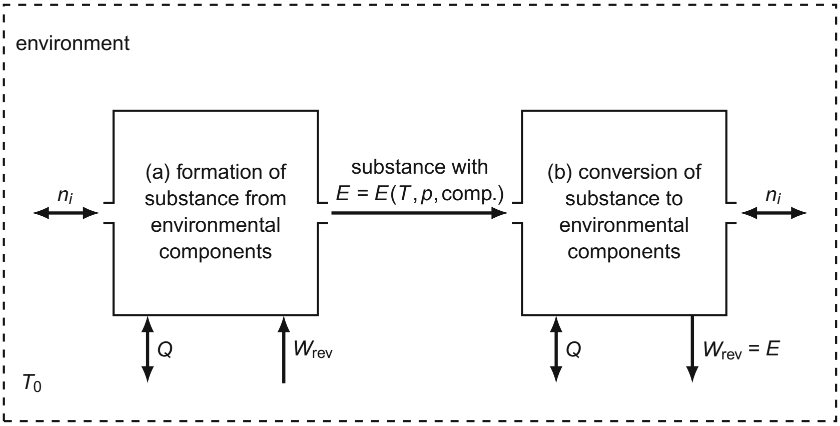


Fig. 1.16 Definition of exergy: reversible cycle process in two coupled open systems exchanging mass and heat with the environment

concept of exergy, we consider two open systems which are connected and together form a closed system (Fig. 1.16). In subsystem (a), a chemical substance is formed from components available at temperature T_0 in the environment through reversible processes. If this substance is transferred to subsystem (b) one can see that a certain amount of useful work $W_{\text{rev}} = E$ can be extracted from converting the substance back to environmental components.

One can show that the exergy of a system can be obtained with

$$E = H - H_0 - T_0(S - S_0) \tag{1.20}$$

where H and S are enthalpy and entropy of the system and H_0 and S_0 the corresponding values in equilibrium at T_0, when no work can be obtained from it in the given environment. The importance of the environment for determination of the exergy of a system or substance is easily understood if one considers that, for example, liquid water with 20 °C cannot perform work in temperate climates while it could do so in colder places such as the Antarctic. The calculation of the exergy therefore requires the definition of appropriate parameters for the environment where the system under consideration operates, in terms of temperature, pressure, and chemical composition. Many different attempts have been undertaken to define such a *reference state* for the environment. Unusual for classical technical thermodynamics, the more advantageous of these approaches consider realistic conditions on Earth, which are quite far from equilibrium, as the reference state. Two examples are given in Table 1.4.

The reference environment suggested by Riekert (1980) appears to be especially suitable for the exergetic analysis of large-scale technical chemical processes as it includes raw materials required for many important base chemicals. Interestingly, it also takes into account that flue gases from combustion processes are abundant in any industrialized economy. Table 1.5 summarizes exergies obtained with this reference environment and compares them with the lower and higher heating values

Table 1.4 Examples for reference environments

	Gaggioli and Petit (1977)		Riekert (1980)	
Conditions	$T_0 = 298.15\,\mathrm{K}$, $p_0 = 1\,\mathrm{atm}$		$T_0 = 298\,\mathrm{K}$, $p_0 = 1.01\,\mathrm{bar}$	
Atmosphere	Constituents	Mole fractions	Constituents	Mole fractions
	N_2	0.7567	N_2	0.8
	O_2	0.2035	O_2	0.2
	H_2O	0.0303		
	Ar	0.0091		
	CO_2	0.0003		
	H_2	0.0001		
Condensed phases	Water (H_2O) Calcium carbonate ($CaCO_3$) Calcium sulfate ($CaSO_4 \cdot 2\,H_2O$)		Water (H_2O) Calcium carbonate ($CaCO_3$) Calcium sulfate ($CaSO_4 \cdot H_2O$) Calcium phosphate ($Ca_3(PO_4)_2$) Sodium sulfate ($Na_2(SO_4)$) Sodium chloride (NaCl)	
Additional components			Flue gas ($p_{CO_2} = 0.2\,\mathrm{bar}$)	

Table 1.5 Specific exergies E of chemical substances at 298 K and 1 bar calculated with the reference environment according to Riekert (1980) and corresponding heating values (*HHV*, *LHV*), required values for enthalpies of formation and entropies taken from Atkins and Paula (2001)

Component	*E*		*HHV*		*LHV*	
	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{MJ\,kg^{-1}}$	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{MJ\,kg^{-1}}$	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{MJ\,kg^{-1}}$
Carbon (C)	394.4	32.9	393.5	32.8	393.5	32.8
Hydrogen (H_2)	237.6	118.8	285.8	142.9	241.8	120.9
Methane (CH_4)	817.9	51.1	890.3	55.6	802.3	50.1
Octane (C_8H_{18})	5325	46.7	5471	48.0	5074	44.5
Glucose ($C_6H_{12}O_6$)	2885	16.0	2808	15.6	2544	14.1
Methanol (CH_3OH)	697.6	21.8	726.4	22.7	638.4	20.0
Ammonia (NH_3)	337.5	19.9	382.6	22.5	316.6	18.6

of several chemical substances. These selected components include carbon, methane, and octane as model components for solid, gaseous, and liquid fossil fuels (see Sect. 5.5), hydrogen as a possible future energy carrier (Sect. 7.2.5), glucose as model component for photosynthesis-based biomass (Sect. 3.4), and methanol and ammonia as examples for large-scale chemical intermediates with high energy content. One can see that the calculated exergies are in many cases very close to the higher heating values of the substances. This is the case for carbon, liquid hydrocarbons, and glucose, while the exergies of hydrogen and methane are closer to the lower heating values of these species. Thus, if conversion of chemical energy to work (or electrical energy) is considered, the exergies of fossil fuels – with the exception of methane – and of biomass can be replaced by their higher heating values with sufficient accuracy.

The energy demand of our societies is to a very large extent based on fossil fuels and biomass. The bigger part of these energy containing substances is employed by combustion to satisfy our demands regarding the heating or cooling of buildings as well as for mobility and transport. In all these cases, the exergy of the starting materials is completely lost as the reaction products and the useful work initially produced from them are eventually dissipated to the environment at ambient temperature.

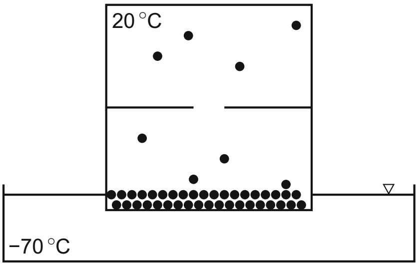
1.3.3 Non-equilibrium Thermodynamics: Complex Behavior and Formation of Structures

Thermodynamics can also be applied to non-equilibrium situations. All open systems with exchange of matter or energy over the system boundary are not in equilibrium, such as a chemical reactor, an organism, or the Earth as a whole. While systems sufficiently close to their equilibrium state exhibit a so-called *linear* behavior, it can be shown that conditions far from equilibrium can be unstable and may evolve to different states that are available to the system (Kondepudi and Prigogine 1998). Given the irreversibility of the processes involved, the boundary conditions of the system are no longer sufficient to determine the exact non-equilibrium state of the system. Three possibilities for system behavior can be distinguished in these cases.

a) The system remains constant in one of the attainable states depending on its previous history (cf. Fig. 1.14),
b) fluctuations between different possible states occur (cf. Fig. 1.11), or
c) the system develops spatially distributed properties.

Surprisingly, non-equilibrium systems are capable of developing order and often complex structures. A very simple example is given in Fig. 1.17 that depicts a closed system filled with a condensable gas in contact with two different temperature reservoirs. One can see that the molecules in this system are no longer randomly distributed as it would be the case in an isolated system, but separate to form a gas phase and a more concentrated condensed phase in the region in contact with the colder reservoir.

Fig. 1.17 Formation of structures in a closed system by exchange of energy



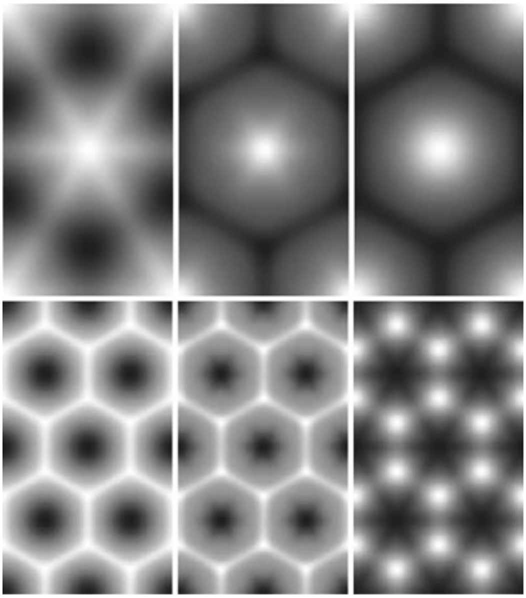


Fig. 1.18 Calculated flow patterns for Rayleigh–Bénard convection in a plane horizontal fluid layer heated from below (Getling and Brausch 2003, published with kind permission of © American Physical Society, 2003, all rights reserved), *dark regions* warm, *light regions* cold

An example for more complex structures is the formation of Rayleigh–Bénard patterns in systems with heat transfer. If a fluid between two parallel plates is heated from below, convection cells (Fig. 1.18) will develop if the temperature gradient in the system becomes high enough. The initially random movement of the molecules in the fluid is thus replaced by a geometrically stable rotation flow caused by the interaction between buoyancy and gravity. Depending on the particular situation, a broad variety of structures can be obtained.

Another well-known example for pattern formation in reacting systems is depicted in Fig. 1.19. Here, patterns of adsorbed oxygen and carbon monoxide on the surface of a platinum catalyst are shown as a function of time. Although the considered stoichiometry is very simple (React. (1.21)) several unusual phenomena occur if a platinum surface is brought into contact with a flow of the reactants CO and O_2.

$$2\,CO + O_2 \longrightarrow 2\,CO_2 \qquad (1.21)$$

In the 1970s it was recognized that oscillations of the reactant and product concentrations occur although all boundary conditions of the system were kept constant (Schüth et al. 1993). This behavior is caused by the periodic reconstruction of the platinum surface under the influence of the adsorbed reacting species. With the advent of modern techniques in electron microscopy it became possible to observe the platinum surface under reaction conditions with great resolution. These observations made by the research group of 2007 Nobel Laureate in Chemistry Gerhard Ertl provided fascinating insight into the remarkably complex spatio-temporal dynamics of this apparently simple chemical reaction (Ertl 2009). The complicated interaction

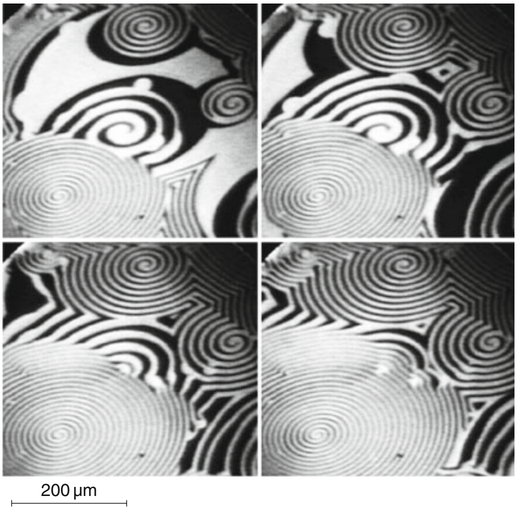


Fig. 1.19 Patterns of carbon monoxide (*light*) and oxygen (*dark*) on a platinum surface (Nettesheim et al. 1993), published with kind permission of © AIP Publishing LLC, 1993, all rights reserved

of surface reaction, platinum reconstruction, and adsorbate diffusion gives rise to patterns moving like spiral waves with front speeds of several $\mu\mathrm{m\,s}^{-1}$.

These structures, as Ertl pointed out in his Nobel lecture (http://nobelprize.org), are reminiscent of similar phenomena found in nature such as the structure of the retina and a leopard fur. Kondepudi and Prigogine (1998) have collected many other examples of these *dissipative structures* that bring order to systems which are far from equilibrium. The basis for the development of order (and thus of states with low entropy) on Earth is the continuous flow of energy from the Sun which drives all these complex processes.

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Chapter 2
Biogeosphere as Environment for Life

The properties of the Earth and especially of the biogeosphere as an environment that has allowed for the development of life and human civilization are discussed in this chapter. The first section describes the position of the Earth in the solar system and the present conditions on Earth as a whole as well in its constituents, e.g. crust, ocean, and atmosphere. The second section deals with the driving forces for changes in the biogeosphere and the resulting developments of the atmospheric composition and the global climate. Finally, the development of life on Earth and of the human civilization are briefly reviewed.

2.1 Planet Earth and the Present Biogeosphere

Earth is part of the solar system and the third of the four so-called inner planets (Fig. 2.1). Characteristic data of the Sun, the planets, as well as of the Moon can be found in Table 2.1. Earth has a mean distance of 149.6×10^6 km from the Sun and a rotational speed of $29.8\,\mathrm{km\,s^{-1}}$ resulting in a rotation period of about 365 d. The average density of the Earth is relatively similar to the values of the other inner planets which all mainly consist of rocks and metals. On the other hand, the four outer planets largely contain light elements and components, e.g. hydrogen, helium, ammonia, and water. As a result, the atmosphere of the outer planets contains mostly hydrogen and helium, while the main atmospheric constituents of the inner planets are nitrogen and carbon dioxide, except for Mercury which has hardly any atmosphere. A unique property of Earth is that its atmosphere contains large quantities of oxygen, a property that has been caused by the evolution of life and decisively determines the conditions on Earth.

The structure of the Earth is depicted in Fig. 2.2. The inner layer is the partly solid and partly liquid core with a radius of about 3470 km that consists mainly of iron and other metals at very high temperature and pressure (cf. Table 2.2). The mantle, located between core and crust, can be considered as an extremely viscous liquid capable of flowing on long timescales. The mantle contains silicate rocks and metals, which results in a higher density than the solid crust. This upper solid layer of the

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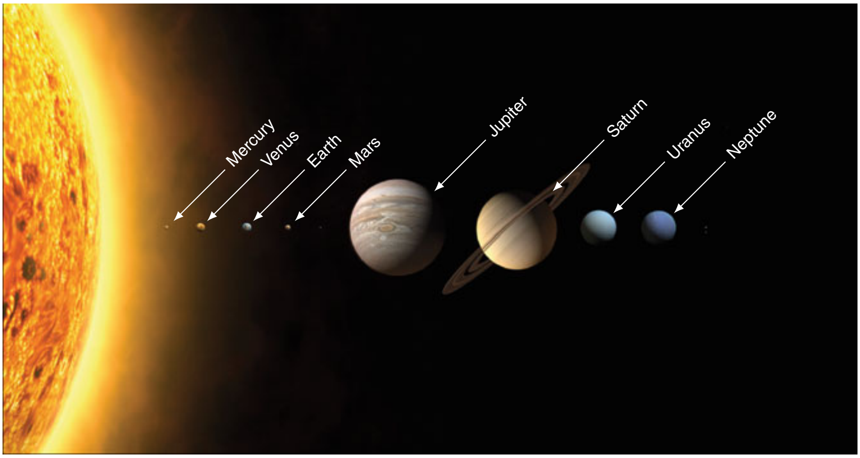


Fig. 2.1 Image of solar system, distances not to scale (http://www.iau.org)

Earth has a thickness of 20–100 km and contributes only a small fraction, 1.2 %, to the total mass of the Earth. Additional layers of the Earth are the ocean with an average thickness of 3.7 km, and the atmosphere. As the density of the atmosphere exponentially decreases with height (see Fig. 2.5), 99 % of its mass is contained in a layer with a thickness of only about 30 km. The atmosphere and ocean together represent less than 0.025 % of Earth's mass.

The *biogeosphere* combines the layers of the Earth where life can exist, i.e. the lower atmosphere, the ocean, and soils and sediments that are part of the crust. Smil (2002) has pointed out that living organisms have invaded the entire ocean, most of the atmosphere – with birds reaching altitudes of more than 10 km and microorganisms even the highest layers of the stratosphere – as well as regions below ground, and the deep-ocean floor down to at least 5 km depth. Although the extent of the biogeosphere is remarkable, these few tens of kilometers form only a very thin layer separating the habitable parts of Earth from the hot interior and outer space. The conditions in the biogeosphere are not only determined by the incoming radiation from the Sun (F_{in}) and the outgoing radiation emitted by Earth's surface (F_{out}) (Fig. 2.2), but also very strongly by the existence of life, as will be shown later.

The average compositions of the whole Earth and of the layers constituting the biogeosphere reveal interesting differences (Table 2.3). While living organisms are mainly composed of the elements carbon, hydrogen, oxygen, nitrogen, sulfur, and phosphorus, it can be seen that some of these elements are only present in minor amounts in the biogeosphere. The Earth crust is composed of silicate rocks with oxygen having the largest mass fraction. The ocean is an aqueous solution of different salts (mostly sodium chloride) with a total concentration of about 3 wt% and contains also trace amounts of dissolved atmospheric gases. The main constituents of the atmosphere are nitrogen and oxygen. These unusually high amounts of free nitrogen and oxygen together with the much lower carbon dioxide fraction than for

Table 2.1 Characteristic data (mean values) of Sun, planets, and Moon, data from Jacobshagen et al. (2000), Hartmann (1994), unless otherwise noted

	Sun	Mercury	Venus	Earth	Mars
Distance from Sun/10^6 *km*		59.9	108.2	149.6	227.7
Orbital period/a[a]		0.2408	0.6152	1.000	1.881
Rotational speed/km s^{-1}		47.9	35.1	29.8	24.2
Rotation period/d	25.5	58.6	243	1.00	1.02
Escape velocity/km s^{-1}	617.6[c]	4.27	10.3	11.2	5.01
Equatorial diameter/km	1 391 400	4878	12 100	12 756	6786
Mass/kg	1.987×10^{30}	3.3×10^{23}	4.87×10^{24}	5.99×10^{24}	6.44×10^{23}
Density/g cm^{-1}	1.4	5.46	5.23	5.52	3.92
Albedo		0.058	0.71	0.30	0.16
Surface temperature/°C	6050	350	480	15	–23
Surface pressure/bar		2×10^{-15}	90	1	7×10^{-3}
Atmosphere	92 % H_2		96 % CO_2	77 % N_2	95 % CO_2
	7.8 % He		4 % N_2[c]	21 % O_2	2.7 % N_2
				1 % Ar	1.1 % Ar
	Jupiter	**Saturn**	**Uranus**	**Neptune**	**Moon**
Distance from Sun/10^6 km	778.3	1429.4	2875.0	4504.3	0.35[b]
Orbital period/a[a]	11.86	29.46	84.01	164.8	27.32d[b]
Rotational speed/km s^{-1}	13.1	9.64	6.81	5441	
Rotation period/d	0.41	0.43	0.7	0.7	27.3
Escape velocity/km s^{-1}	59.4	35.5	21.4	23.4	2.4
Equatorial diameter/km	142 796	120 000	50 800	46 300	3476
Mass/kg	1.91×10^{24}	5.57×10^{24}	8.66×10^{24}	1.03×10^{24}	7.35×10^{22}
Density/g cm^{-1}	1.31	0.70	1.3	1.66	3.35[c]
Albedo	0.34	0.34	0.34	0.29	0.11[c]
Surface temperature/°C	–150	–175	–225	–220	–75
Surface pressure/bar	$\gg 100$	$\gg 100$	$\gg 100$		10^{-14}
Atmosphere	89 % H_2	97 % H_2	85 % H_2		
	11 % He	3 % He	15 % He		

[a] Except moon
[b] Relative to Earth
[c] Fact sheets on http://nssdc.gsfc.nasa.gov

the other inner planets (Table 2.1) are caused by living organisms, namely through photosynthesis (cf. Sect. 3.4).

Figure 2.3 shows some important interactions between the constituents of the biogeosphere. The *hydrosphere* is the combined mass of water found on Earth, i.e. the ocean, freshwater, groundwater, and ice. The *lithosphere* is the outer rocky shell of the planet, including the crust and the uppermost mantle. The *biosphere* as the entirety of all living organisms interacts with the hydrosphere, lithosphere, and atmosphere. Climate, i.e. the average weather conditions including temperature, precipitation,

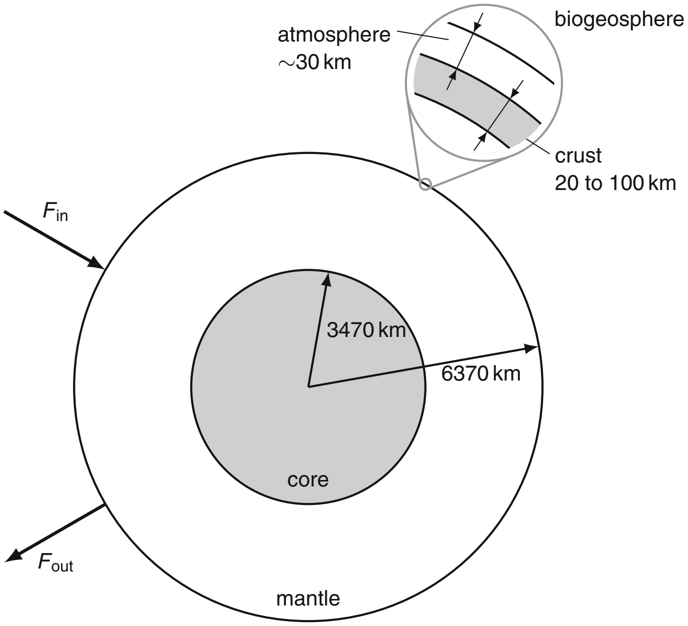


Fig. 2.2 Structure of Earth

Table 2.2 Properties of Earth layers, data from Cattermole (2000), Krauskopf (1979)

Layer	Earth	Core	Mantle	Crust	Ocean	Atmosphere
Thickness (radius)/km	6370	3470	2850	20–100	3.7[a] ($\leq$11)	30[b]
Mean density/kg m^{-3}	5520	10 700	4500	2800	1027	1.2[c]
Mass/kg	5.98×10^{24}	1.87×10^{24}	3.97×10^{24}	7.08×10^{22}	1.41×10^{21}	5.12×10^{18}
Mass fraction/ %	100	31.6	67.2	1.20	0.024	0.00009
Temperature/°C	–	3000–4000	1000–3000	15–400	15	15[c]
Pressure/bar	–	3.8×10^{6}[d]	1.4×10^{6}[d]	1[c]	1[c] ($\leq$ 1100)	1[c]

[a] Average value

[b] Contains $\geq$99 % of atmosphere mass

[c] At sea level

[d] Maximal values

wind etc. mainly concerns the atmosphere and the hydrosphere. On the other hand, the interaction between atmosphere and lithosphere leads to decomposition and erosion of solid components. Finally, sedimentation and formation of reservoirs mainly takes place at the interface between hydrosphere and lithosphere.

The conditions in the biogeosphere are obviously influenced by the radiative energy that the Earth receives from the Sun (Chap. 3). Physical and chemical processes taking place in the ocean, atmosphere and on the land surface also strongly

Table 2.3 Composition (mass fractions) of whole Earth (Schlesinger 1997), Earth crust (Krauskopf 1979), ocean (Krauskopf 1979), and atmosphere (Schlesinger 1997, additionally assuming a mean water concentration of 4000 ppm), bold elements are the most important constituents of living organisms (CHONSP)

Rank	Whole Earth	%	Earth crust	%	Ocean	%	Atmosphere	%
1	Iron	35	**Oxygen**	46.4	**Oxygen**	86.0	**Nitrogen**	75.3
2	**Oxygen**	30	Silicon	28.2	**Hydrogen**	11.0	**Oxygen**	23.4
3	Silicon	15	Aluminum	8.1	Chlorine	1.88	Argon	1.28
4	Magnesium	13	Iron	5.4	Sodium	1.08	**Hydrogen**	0.03
5	Nickel	2.4	Calcium	4.1	Magnesium	0.13	**Carbon**	0.02
6	**Sulfur**	1.9	Sodium	2.4	**Sulfur**	0.09		
7	Calcium	1.1	Magnesium	2.3	Calcium	0.04		
8	Aluminum	1.1	Potassium	2.1	Potassium	0.03		
9			Titanium	0.50	**Nitrogen**	0.02		
10			**Hydrogen**	0.14				
11			**Phosphorus**	0.11				
12			Manganese	0.10				
13			Fluorine	0.07				
14			Barium	0.05				
15			Strontium	0.04				
16			**Sulfur**	0.03				
17			**Carbon**	0.02				

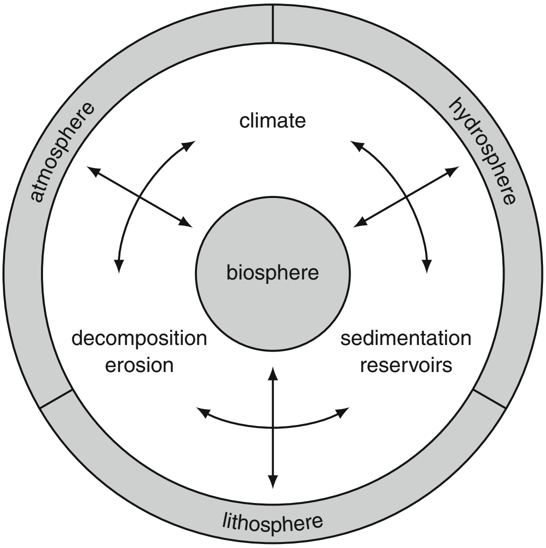


Fig. 2.3 Earth's biogeosphere and the interactions of its constituents, inspired by a brochure of the International Union of Geological Sciences (IUGS), http://iugs.org/uploads/images/PDF/12_earthandlife.pdf

determine the chemical composition in the different compartments and the energy balance of the Earth. However, the most powerful force for changes during Earth history and for maintaining the beneficial current conditions on our planet has been life, as will be discussed in the following section.

2.2 Historical Development of the Biogeosphere

The biogeosphere has undergone a long development over at least 3.5 Ga with drastic changes in the conditions on Earth. These transformations were driven by several factors the most important of which was the evolution of life. The composition of Earth's atmosphere is currently very different from the reconstructed initial state after formation of the Earth and development of the first organisms. At the same time the climatic conditions were subject to alterations as the Earth's energy balance is strongly influenced by the presence of some atmospheric constituents. Life is the key player in the Earth system as it not only continuously alters the global conditions, but has, until now, also been able to adapt itself to the new constraints and to evolve consistently new, higher forms. Recently, man – and especially the modern industrialized civilization – has become an additional driver which has a dramatic impact on global ecosystems and climate at an unprecedented time rate of change.

2.2.1 Formation of Earth and Driving Forces for Change

Earth as a part of the solar system is about 4.5 Ga old (Dalrymple 1991). Thus, it is much younger than our galaxy which has an estimated age of 13.2 Ga (Frebel et al. 2007) and was formed relatively soon after the universe originated in the *Big Bang* some 13.75 Ga ago (Hinshaw et al. 2009). Planets are believed to have grown in the solar nebula from agglomeration of dust and small bodies, so-called *planetesimals* (Schlesinger 1997). The early Earth most probably did not have any atmosphere as the energy released during collisions of planetesimals and by radioactive processes in its interior lead to the melting of the Earth's constituents. Even if there had been an atmosphere, it must have been completely lost as the Moon was formed after collision of the Earth with a body of almost the size of Mars causing the melting of both the impactor and Earth's mantle (Wayne 2009).

After subsequent cooling down, a solid crust was then formed and a new atmosphere mainly consisting of CO_2, N_2 and H_2O developed from outgassing from the inner Earth and from impacting ice-containing bodies such as comets (Wayne 2009). Although the ocean might have appeared as early as 200 Ma after formation of the Earth, it is very likely that repeated vaporization of part or even the entire mass of liquid water was caused by impacts of large bodies until around 3.8 Ga before present (Smil 2002). Only after that period of *heavy bombardment* could life have been formed on Earth, most probably not later than 3.5 Ga ago (Wilde et al. 2001).

However, even after the initial dramatic incidents, conditions on Earth have been subject to considerable changes caused by several different mechanisms (Table 2.4). The most important processes on the early Earth were inorganic chemical reactions of the large amounts of gaseous carbon dioxide with rocks to form carbonates. Before the evolution of photosynthesis, these weathering reactions were the primary mechanism causing the initially very high atmospheric CO_2 partial pressure of about 10 bar to decrease (cf. Fig. 1.7). On the other hand, volcanoes permanently release gaseous components, the most important of which are H_2O, CO_2, and SO_2, to the atmosphere. The movement of tectonic plates, which is mainly responsible for the volcanic activity, may have had additional effects on the conditions in the biogeosphere. For example, an increased rate of weathering reactions during geologic times with a higher fraction of continents placed in the tropics leads to enhancement of the CO_2 uptake from the atmosphere.

Other driving forces for change are related to the radiative energy received from the Sun. According to standard stellar models, stars like the Sun gradually increase their radiance with time, resulting in a relative intensity of only 70 % during the early Earth's history. In addition to this gradual rise of irradiation, the movement of the Earth around the Sun leads to several periodic variations called *Milankovich cycles* which include changes of the Earth's precession, the elliptical orbit and the angle of Earth's axial tilt. These cycles lead to periodic alterations of the overall solar radiation reaching Earth on time scales of tens to hundreds of thousand years.

Finally and most importantly, the formation and further evolution of life has brought about additional changes that include the transformation of the atmospheric conditions as well as the coverage of large parts of the continents with land plants. Although causing only detrimental climate effects on a relatively short time scale, impacts of large extraterrestrial objects may have played an important role during the evolution of life as these incidents not only lead to mass extinction of species but probably also triggered the subsequent development of larger biodiversity levels

Table 2.4 Drivers for change of conditions in the biogeosphere

Mechanism	Effects
Inorganic weathering	Conversion of gaseous CO_2 to solid carbonates
Volcanism	Release of gaseous components to the atmosphere
Plate tectonics	Movement of tectonic plates on long time scales
Increasing solar luminosity	Changes of radiative energy balance
Changes in orbital movement and axial position	Periodic alterations of amount and location of solar radiation
Formation of life	Changes in atmospheric composition and global energy balance
Impacts of large space objects	Short-term climate changes, extinction of species
Industrialization	Global impact on land use and massive release of greenhouse gases

(Smil 2002). Finally, man has appeared on the global scene and the capabilities of modern societies together with the rapidly growing population (see Sect. 2.2.5) have resulted in ongoing changes of the biogeosphere that now concern the entire Earth.

2.2.2 Atmosphere

The early atmosphere on Earth was in a reduced state and consisted mostly of carbon dioxide, nitrogen, and water together with minor amounts of hydrogen and carbon monoxide. Inorganic weathering reactions such as the conversion of diopside to carbonates (React. 2.1) lead to a removal of CO_2 from the atmosphere (Wayne 2009).

$$\mathrm{CaMgSi_2O_6 + CO_2 \longrightarrow MgSiO_3 + CaCO_3 + SiO_2} \tag{2.1}$$

The first organisms after the formation of life were most probably methanogenic bacteria converting hydrogen with carbon dioxide to methane and water in anaerobic metabolic pathways. The first photosynthetic reactions were based on carbon dioxide and either hydrogen or hydrogen sulfide and did not generate oxygen (*anoxic* photosynthesis).

Free oxygen in the atmosphere before the evolution of life could have been formed only to a minor extent by inorganic photolysis of water vapor. After the development of the oxygen-producing (*oxygenic*) photosynthesis reaction (see Sect. 3.4) the oxygen levels in the atmosphere rose until present-day levels were eventually reached. However, it took some time before O_2 started to accumulate in the atmosphere as the released oxygen was initially consumed by reduced atmospheric components (CO, H_2), reduced species in the ocean (Fe^{2+}, S^{2-}), and reduced minerals such as pyrite (FeS_2). Figure 2.4 shows that the formed oxygen initially lead to *banded iron formations*, a characteristic type of rock containing hematite (Fe_2O_3) or magnetite (Fe_3O_4). After atmospheric oxygen started to accumulate around 2 Ga before present, or even as early as 2.4 Ga ago according to Buick (2008), so-called *red beds* occurred. These are iron oxide containing minerals that indicate aerobic terrestrial weathering. This process consumed the major part of O_2 from photosynthesis until the atmospheric oxygen concentration started to rise significantly. Overall, it is believed that 98 % of the released oxygen is now bound as iron oxides or sulfate, whereas only 2 % remained in the atmosphere.

The structure of the atmosphere is depicted in Fig. 2.5. Gravitational forces keep the gaseous constituents of the atmosphere close to Earth's surface. The atmospheric pressure p strongly decreases with altitude z as the mass of the overlying atmosphere becomes smaller. The hydrostatic equation (Eq. (2.2)) describes this relationship.

$$p = p_0 \exp \int_0^z \frac{gM}{RT}\,\mathrm{d}z \tag{2.2}$$

Here, p_0 is the pressure at surface level, g the acceleration of gravity, M the average molar mass of air, R the gas constant (8.314 J $\mathrm{mol^{-1}K^{-1}}$) and T the temperature. This

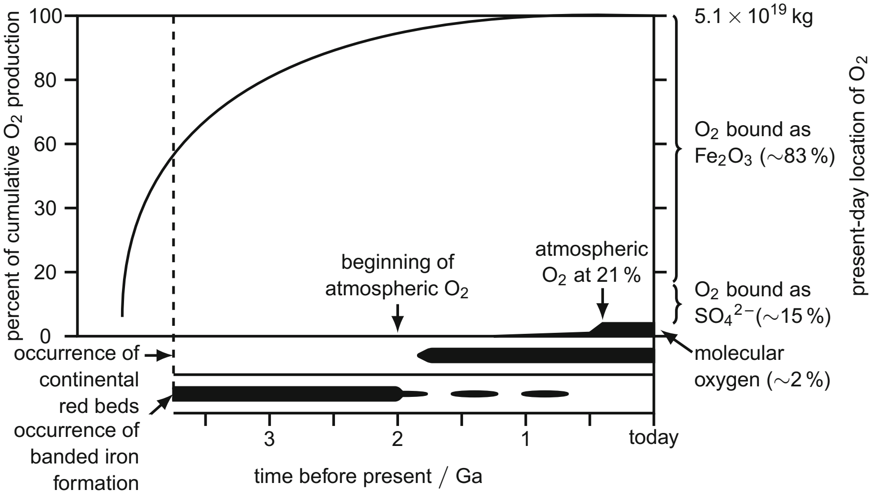


Fig. 2.4 Cumulative history of O_2 released by photosynthesis through geologic time, after Schlesinger (1997)

equation assumes that the atmosphere behaves like a single gas with a mean molar mass, although in reality several gases with different masses occur. However, the mixing processes in the atmosphere below an altitude of about 100 km are efficient enough to achieve a uniform composition (Coe 2009).

The thermal structure of the atmosphere is relatively complicated (Fig. 2.5). In the lowest layer above the Earth's surface (the *troposphere*), the temperature almost linearly decreases by about 6.5 K km^{-1} until a first minimum (*tropopause*) is reached at a height of 10 km. The *stratosphere* is the second atmospheric layer between 10 and 50 km, where the temperature gradually increases to a maximum of about 0 °C at the *stratopause*. This temperature inversion is caused by the photolytic splitting of O_2 by ultraviolet solar radiation and the resulting formation of ozone (O_3, Reacts. (2.3) and (2.4)).

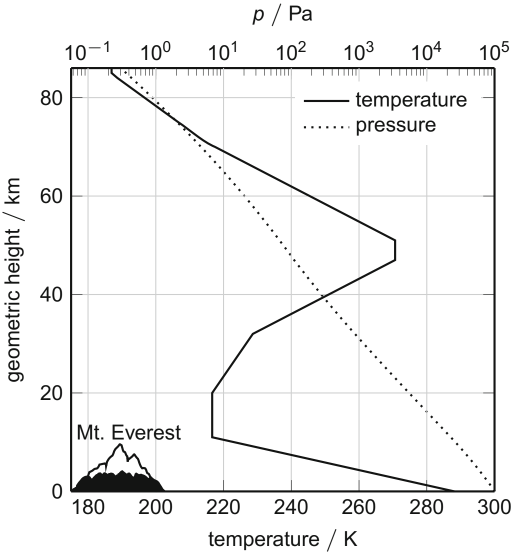
$$O_2 \longrightarrow 2\,O \tag{2.3}$$

$$2\,O + 2\,O_2 \longrightarrow 2\,O_3 \tag{2.4}$$

This overall reaction effectively absorbs ultraviolet radiation from the Sun (Fig. 3.3) and is thus a protective shield for organisms living on the land surface (Sect. 2.2.4).

The third layer of the atmosphere is called *mesosphere*, which extends to about 90 km above surface level. Here, the temperature decreases again. The thermal structure of the troposphere is also responsible for the global circulation patterns of the atmosphere (Fig. 2.6). Due to the large amounts of solar radiation received at the equator (see Sect. 3.3), warm air masses that contain much water vapor rise there. Upon cooling at higher altitudes, precipitation occurs and the now relatively dry air moves away from the equator. At approximately 30N and 30S latitude, the air

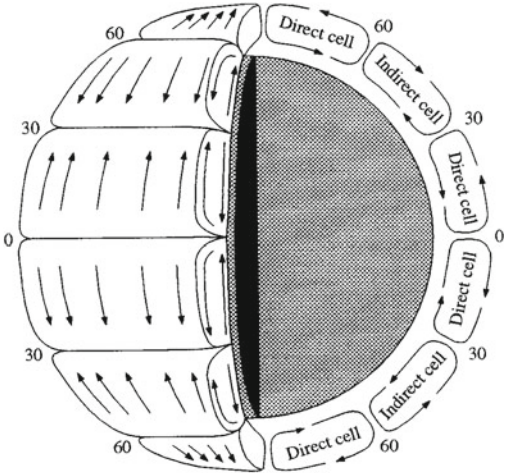
Fig. 2.5 Temperature and pressure profile of the atmosphere to 86 km as defined by the US Standard Atmosphere (1976)



masses sink to the surface and form characteristic direct patterns, so-called *Hadley* cells. Similar patterns also occur in the polar regions, and the two direct tropical and polar cells drive an indirect circulation pattern known as *Ferrel* cell at 30–60N and 30–60S. As a result of these intensive circulation processes, the tropospheric air in the Northern and Southern Hemisphere mixes within a few months (Schlesinger 1997).

Table 2.5 summarizes the average concentrations of atmospheric constituents, their total mass, and their mean residence time. Most of these species are quite uniformly distributed in the atmosphere. This is the case for the main atmospheric

Fig. 2.6 Global patterns of circulation showing surface patterns (*left hand side*) and vertical patterns (*right hand side*), from Schlesinger (1997), published with kind permission of © Academic Press, 1997, all rights reserved



components, nitrogen and oxygen, and all other gases with a residence time of at least a few years. The behavior of water vapor is very different as it has a residence time of only about 10 days (Schlesinger 1997). Therefore, the water vapor concentration shows large spatial and temporal variations. Additionally, the upper parts of the atmosphere above 10 km contain only minor amounts of water due to their relatively low temperatures. Another example of a component with significant variations is ozone, which develops a characteristic profile as a function of altitude and may decline strongly at certain locations due to anthropogenic activities (see Sect. 4.7).

Table 2.5 Global average concentrations of atmospheric constituents, data from Schlesinger (1997) unless otherwise noted

Compounds	Formula	Concentration[a,b]	Residence time/a	Total mass/kg
Major constituents/vol %				
Nitrogen	N_2	77.698	2.4×10^7[d]	3.87×10^{18}
Oxygen	O_2	20.863	4000[d]	1.19×10^{18}
Argon	Ar	0.930		6.59×10^{16}
Water	H_2O	0.4	0.025	1.3×10^{16}[a]
Parts-per-million constituents/ppm $= 10^{-6}$				
Carbon dioxide	CO_2	396[f]	3.6[d]	3.08×10^{15}[f]
Neon	Ne	18.1		6.49×10^{13}
Helium	He	5.22		3.70×10^{12}
Methane	CH_4	1.80[f]	12[c]	5.11×10^{12}[f]
Krypton	Kr	1.14		1.69×10^{13}
Parts-per-billion constituents/ppb $= 10^{-9}$				
Hydrogen	H_2	508		1.82×10^{11}
Ozone	O_3	390		3.3×10^{12}[e]
Nitrous oxide	N_2O	325[f]	114[c]	2.53×10^{12}[f]
Xenon	Xe	87		2.02×10^{12}
Parts-per-trillion constituents/ppt $= 10^{-12}$				
Methyl chloride	CH_3Cl	620	1.0[c]	5.53×10^9
CFC 12	CCl_2F_2	527[f]	100[c]	1.13×10^{10}[f]
Carbonyl sulfide	COS	500		5.30×10^9
CFC 11	CCl_3F	235[f]	45[c]	5.71×10^9[f]
Ammonia	NH_3	100[e]		3×10^{10}[e]
Methyl bromide	CH_3Br	11	0.7[c]	1.84×10^8

[a] Original values assuming dry atmosphere with molecular weight of 28.97 g mol^{-1} modified taking into account mass of water vapor (Trenberth and Smith 2005) corresponding to average water concentration of 0.4 vol %

[b] Volume fractions

[c] IPCC (2007)

[d] Own estimates based on reservoirs and transfer flows (cf. Chap. 4)

[e] Hartmann (1994)

[f] Updated 2014

Table 2.6 Global emissions of aerosols, from Schlesinger (1997), after Jonas et al. (1995)

Natural sources	Flow/Mt a^{-1}	Anthropogenic sources	Flow/Mt a^{-1}
Primary aerosols		Primary aerosols	
Soil dust	1500	Industrial particles	100
Sea salt	1300	Soot	20
Volcanic dust	33	Particles from forest fires	80
Organic particles	50		
Secondary aerosols		Secondary aerosols	
Sulfates from organic sulfides	90	Sulfates from SO_2	140
Sulfates from SO_2	12	Organic condensates	10
Organic condensates	55	Nitrates from NO_x	36
Nitrates from NO_x	22		
Sum natural sources	3070	Sum anthropogenic sources	390

Table 2.5 also contains values for several trace gases that are relevant for Earth's radiative energy balance (Sect. 3.2). The concentration of some of these components has strongly risen during the last decades (e.g. CO_2, CH_4, N_2O). Others are produced synthetically and did not occur in the pre-industrial atmosphere (chlorofluorocarbons such as CCl_2F_2). The latter species are chemically inert in the troposphere and are able to mix into the stratosphere, where they contribute to ozone depletion by catalytic action.

In addition to gases, large quantities of small solid particles or liquid droplets, so-called *aerosols*, are present in the atmosphere (Table 2.6). These particles, which are often transported over long distances, can be subdivided into primary and secondary aerosols. *Primary* aerosols are particles that are emitted to the atmosphere as solid particles, e.g. soil dust by wind erosion, dust from volcanoes, or industrial particles especially from coal-fired power plants. *Secondary* aerosols are formed in the atmosphere from volatile components. One example is the natural formation of sulfates from gaseous organic sulfides such as dimethyl sulfide ($(CH_3)_2S$). These sulfate aerosols play an important role as cloud condensation nuclei (see Sect. 4.5).

2.2.3 Climate

Climate is the average state of the atmosphere (temperature, precipitation, pressure, wind speed etc.) observed over long time periods, e.g. several years or decades. In contrast, weather comprises the short-term atmospheric conditions that are relevant for hours or days. The *climate system* consists of the atmosphere, the ocean, the cryosphere (ice on land and ocean), the land surface, and the biosphere. This complex system is determined by several factors the most important of which are the incoming solar radiation and the composition of the atmosphere, especially regarding species able to absorb infrared radiation (Chap. 3). Solar radiation gradually increases over very long time periods, while periodic fluctuations occur due to the movement of the Earth around the Sun. The composition of the atmosphere is – as previously discussed – influenced by inorganic reactions, biotic processes, and most recently through anthropogenic activities.

The simplified reconstructed development of the average global temperature since the formation of Earth as well as a projection for the future are shown in Fig. 2.7. The early Earth was very hot, but rapid cooling occurred and liquid water was formed 4 Ga ago or earlier. Although the solar radiation at that time was lower than today, the temperatures remained higher than at present, most probably caused by very high carbon dioxide concentrations that trapped infrared radiation. CO_2 consuming processes (weathering, photosynthesis) lead to a significant decrease of the global temperature until glaciations – supposedly even worldwide – occurred for certain periods of time. Since about 1 Ga before present, the temperature has shown a rising tendency, probably caused by the increasing solar irradiation at already relatively low carbon dioxide concentration levels. For the long-term development, one can therefore expect the global temperature to rise significantly, especially since there is little capacity for further cooling through reduction of CO_2 concentrations (Wayne 2009).

The temperature depicted in Fig. 2.7 is to a large extent based on geophysical models and only partly on experimental observations. On shorter time scales, a broad range of paleoclimatological methods allows for the relatively precise reconstruction of climatic conditions. These methods are comprised of the investigation of sediments and ice cores, chemical signatures of certain elements in minerals, isotopic ratios (especially of oxygen), investigation of fossil soil and organisms, as well as tree rings from living plants for the very recent developments. Figure 2.8 shows average atmospheric surface temperatures in the Northern Hemisphere for the last million years and the last ten thousand years, respectively. One can see that strong temperature fluctuations of up to 7 K occurred during the last million years and that temperature changes took place within a period of only a few thousands of years.

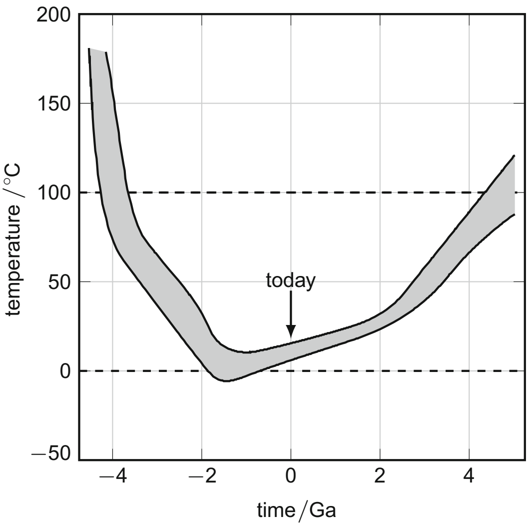


Fig. 2.7 Estimated development of temperature at sea level since the formation of Earth and future prediction, after Schönwiese (2008)

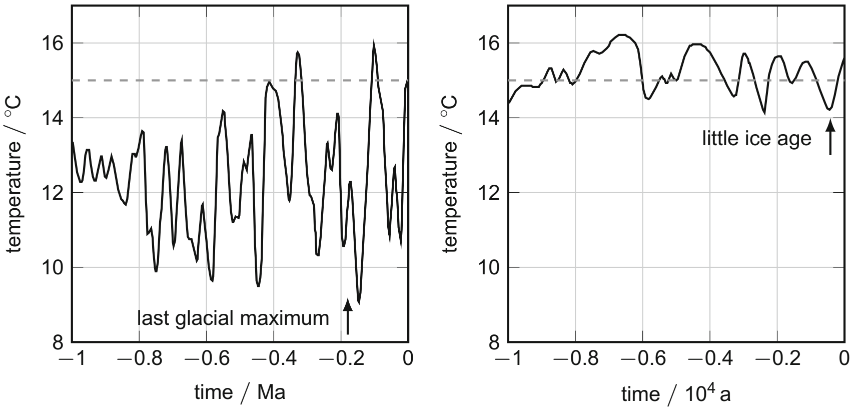


Fig. 2.8 Reconstruction of average surface temperatures in the Northern Hemisphere during the last million years (*left*) and the last ten thousand years (*right*), *dashed lines*: current average global surface temperature, data from Schönwiese (2008)

Overall, the climate in the Northern Hemisphere was much colder than today, with massive glaciations periodically covering large parts of North America and Northern Europe. It has been estimated that Northern Germany, which was predominantly ice-covered during the *last glacial maximum* about 18 000 a ago, had an average yearly temperature of around −20 °C (Schönwiese 2008), more than 25 K lower than today.

In contrast, the temperatures during the last 10 000 years appear to have remained relatively constant around 15 °C (Fig. 2.8, right). Nevertheless, the observed temperature variations of no more than ±1 K were responsible for quite significant local climate changes. During the *medieval climate optimum*, around 1000 a before present, it was possible to colonize the south of Greenland. However, the following *little ice age* – the period between the 14th and the 19th century – brought much colder climates to Europe and North America with crop failure and long, harsh winters. It has to be noted that these considerable climate changes correspond to average surface temperature differences in the Northern Hemisphere of less than 1.5 K.

The systematic study of climatic trends through direct observations started after the development of instruments, e.g. for temperature and pressure measurements. Today, a global network of meteorological stations is available which are assisted by satellite-based measurements. These observations allow for the precise assessment of climatic alterations both locally and as a global average. Figures 2.9 and 2.10 show the development of average summer air temperatures and summer precipitation in Europe between 1901 and 2000 as examples. It can be seen that the regions with the strongest warming (>1.5 K) are located in the south of France, Spain, and around Austria. On the other hand, a slight temperature decrease occurred in some regions of Russia. The temperature trends of the European winter temperature are relatively similar to these patterns. The development of the average summer precipitation (Fig. 2.10) shows that some regions like Portugal, Spain, and Poland received

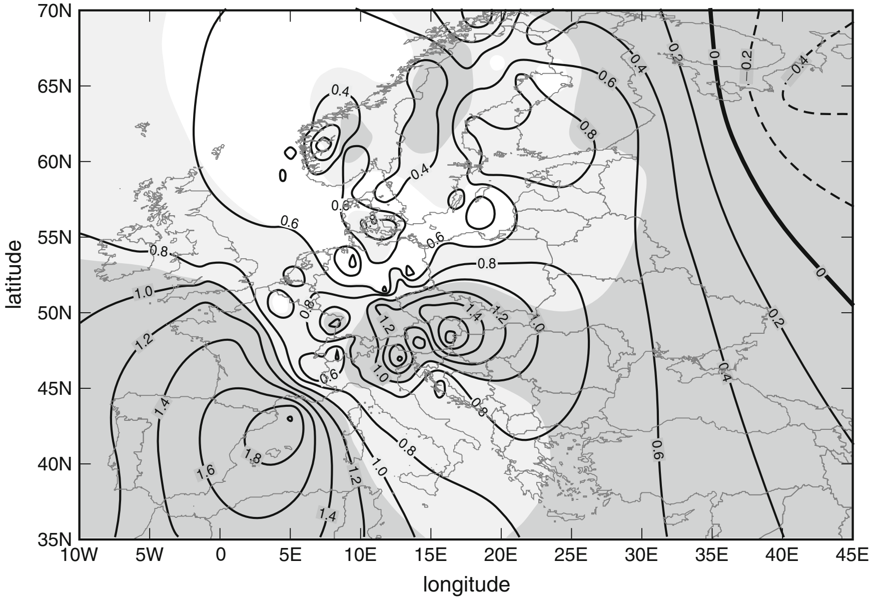


Fig. 2.9 Linear trends of average summer air temperatures in K at sea level in Europe between 1901 and 2000 (Schönwiese 2008), *gray*: >99 % significance, *lightgray*: >85 % significance, *dashed lines*: temperature decrease

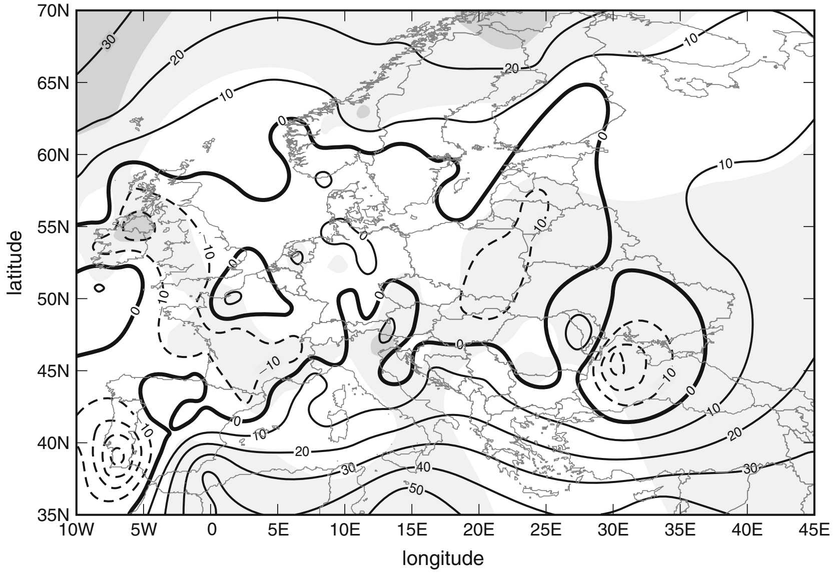


Fig. 2.10 Linear trends (in %) of average summer precipitation in Europe between 1901 and 2000 (Schönwiese and Janoschitz 2008), *gray*: >95 % significance, *lightgray*: >70 % significance, *dashed lines*: decreased precipitations

less rainfall while precipitation increased in Northern Europe, Southern Italy, and Greece. On the contrary, the corresponding trend for winter (not shown) reveals slightly increased rainfall for Central Europe.

The climate system of the Earth shows a complex spatio-temporal behavior. Even during phases with relatively constant average global conditions, significant local variations can occur. In addition to the factors summarized in Table 2.4, the climate is also influenced by atmospheric (see Fig. 2.6) and oceanic circulation. Warm water masses in the *gulf stream* and its extension towards Europe are responsible for higher temperatures in coastal areas of Ireland, Great Britain, and Norway than would exist in the absence of this ocean current. Although the resulting temperature differences might be only on the order of 1 K, the effects on vegetation, agriculture and overall habitability of the respective region are quite noticeable. One should keep these facts in mind for the later discussion of the current and predicted future impact of anthropogenic activities on the climate of the Earth.

2.2.4 Life

Life on Earth comprises all living species such as microorganisms, fungi, plants, and animals. All of these very different living systems have the ability to respond to outer stimuli, to grow, develop and reproduce, to maintain themselves in a stable, favorable state, and to adapt – through natural selection – to their changing environment over successive generations. Organisms are open systems that exchange energy and matter with their surroundings. Viruses are organisms at the edge of life as they have no metabolism of their own and are not able to reproduce autonomously without the aid of a host organism.

The smallest unit of a living system is a cell and organisms can be classified into unicellular and multicellular types. Depending on the kind and complexity of cells, simpler *prokariotic* and more evolved *eukariotic* organisms, the cells of which have a nucleus and so-called organelles, can be distinguished. Prokaryotes are in most cases unicellular organisms such as bacteria and archea. Eukaryotes have a cell nucleus which contains the genetic material and several other cellular substructures, mostly surrounded by membranes, i.e. layers with tailored permeability for molecules and/or ions. These organisms appear as unicellular microorganisms but also as multicellular fungi, plants, and animals.

The energy and mass balance of organisms can be driven by a remarkably broad variety of metabolic pathways. Basically, one can distinguish between *autotrophic* and *heterotrophic* organisms. Autotrophs employ energy from the environment either from sunlight (photoautotrophs) or from simple inorganic compounds (chemoautotrophs) and use it to produce more complex and energy-rich carbon-containing molecules. These mechanisms are the core of primary production of organic molecules and the basis of all food chains. Heterotrophs rely on organic carbon substrates produced by autotrophs. Photoheterotrophs use energy from sunlight, but require organic carbon for growth, whereas chemoheterotrophs such as fungi and animals need carbon-containing molecules both as energy and carbon source.

The metabolism is the overall chemistry taking place in organisms to maintain life. It can be grouped into metabolic pathways, i.e. complex series of chemical reactions often accelerated and controlled by organic catalysts, so-called enzymes. Key components in metabolic pathways are comprised of proteins, carbohydrates, lipids, nucleotides, and many other macromolecules. The central unit of intracellular energy transfer is adenosine triphosphate (ATP) which releases high amounts of energy during hydrolysis to adenosine diphosphate (ADP). Probably the most important development during the evolution of life on Earth was oxygen-producing photosynthesis. This process allows organisms to obtain carbohydrates (e.g. glucose $C_6H_{12}O_6$) from carbon dioxide and water under irradiation of sunlight. The energy contained in glucose is employed via *glycolysis*, another central metabolic pathway taking place in almost all organisms, to build up ATP and other energy carriers.

The myriad of chemical processes necessary for maintaining life, growth of organisms, and their reproduction requires the storage of information and mechanisms for its transmission. All these instructions are encoded in deoxyribonucleic acid (DNA), a long nucleotide-based polymer in form of a double-stranded helix. Remarkably, this type of molecule is composed of only four structural elements, adenine, cytosine, guanine, and thymine. These nucleobases form the DNA macromolecule together with sugar and phosphate groups and the sequence of the four bases contains the genetic information. Decoding takes place via various types of ribonucleic acid (RNA), a macromolecule similar to DNA, but single-stranded and containing uracil rather than thymine as the fourth nucleobase. As a result, all proteins composed of 20 amino acids can be synthesized, which is necessary for the proper function and reproduction of organisms.

Changes in the DNA sequence, caused by errors occurring during DNA replication, by radiation, chemicals, or viruses, are called *mutations*. Depending on the position and severity of the alterations, mutations may have either no effect or give rise to modifications of the cellular chemistry. As many of the mutations have detrimental effects, organisms have developed repair mechanisms to maintain their functionalities. However, mutations can also have positive effects on organisms and are the basis for continuous *evolution* of life. In a changing environment, some mutations of organisms are preferred over others by natural selection. Apparently, these adaptive processes are extremely efficient as life has encountered not only dramatic alterations of environmental conditions during Earth's history, but has also come close to extinction during several occasions such as severe global glaciations and impacts of large extraterrestrial bodies (Smil 2002).

There is general consensus that life has developed over long time spans from primitive beginnings to more evolved and intricate forms. Darwin was among the first to describe this evolution as *tree of life* visualizing the common origin and subsequent branching of species through time. Today, modern classifications of this type are called *phylogenetic* trees which are based on the genetic information contained in organisms. Figure 2.11 shows such a diagram proposed by Woese et al. (1990) who defined archea as a new domain of life independent of bacteria.

This genetically based analysis successfully supports the traditional way to reconstruct the historic evolution of life based on the fossil record. Despite tremendous

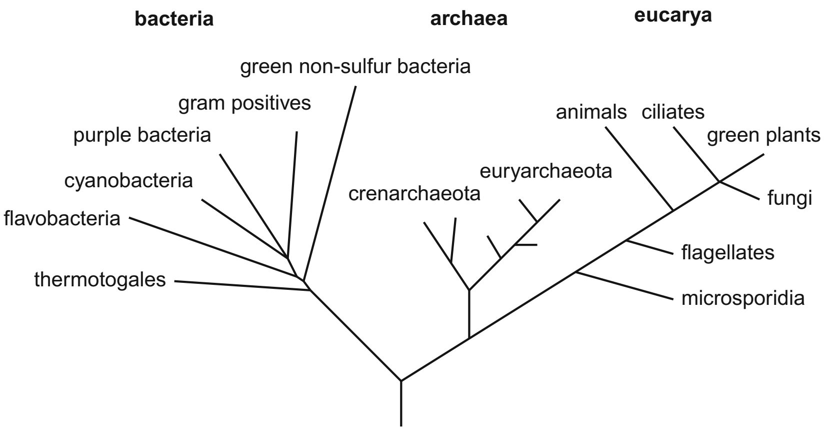


Fig. 2.11 Universal phylogenetic tree based on RNA sequence comparisons, after Woese et al. (1990), simplified

research effort, there is still no generally accepted theory explaining how life on Earth could have formed from inanimate matter. Although elements of the overall process such as the formation of organic molecules and membrane-like structures are quite well understood, there is no consensus about how self-replicating processes might have evolved. Nevertheless, life must have been formed relatively early in Earth's history (Fig. 2.12) as the oldest fossil objects are believed to be microorganisms generated 3.5 Ga before present (Wilde et al. 2001). These already quite complex living organisms must have required some time for development, thus life probably occurred soon after the end of the heavy bombardment about 3.8 Ga ago. During the Archean, simple life forms dominated the biosphere with methanogens, and other species employing several variations of photosynthesis, being present. At the beginning of the Proterozoic, cyanobacteria were already the most important species (Smil 2002). Thus, the oxygen concentration in the atmosphere began to rise soon (Buick 2008).

The appearance of free oxygen in the atmosphere (the *great oxygenation event*) was a milestone in Earth's history when a change from reducing to oxidizing conditions in the biosphere occurred. This had dramatic consequences for those species relying on anaerobic metabolic pathways, like methanogenic bacteria or photosynthetic sulfur bacteria, which were poisoned by O_2 and could survive only in niche habitats. On the other hand, atmospheric oxygen allowed for the development of the ozone layer which protects life from harmful ultraviolet radiation outside the ocean. Moreover, more complex eukariotic cells appeared around 1.8 Ga before present which were the basis for superior multicellular life forms (Schlesinger 1997). At the end of the Proterozoic, algae and first animals such as sponges already existed.

The Phanerozoic, the current eon in the geologic timescale, started about 540 Ma ago with the relatively sudden appearance of many new life forms during the *Cambrian explosion*. Land plants, complex multicellular eukaryotes obtaining their

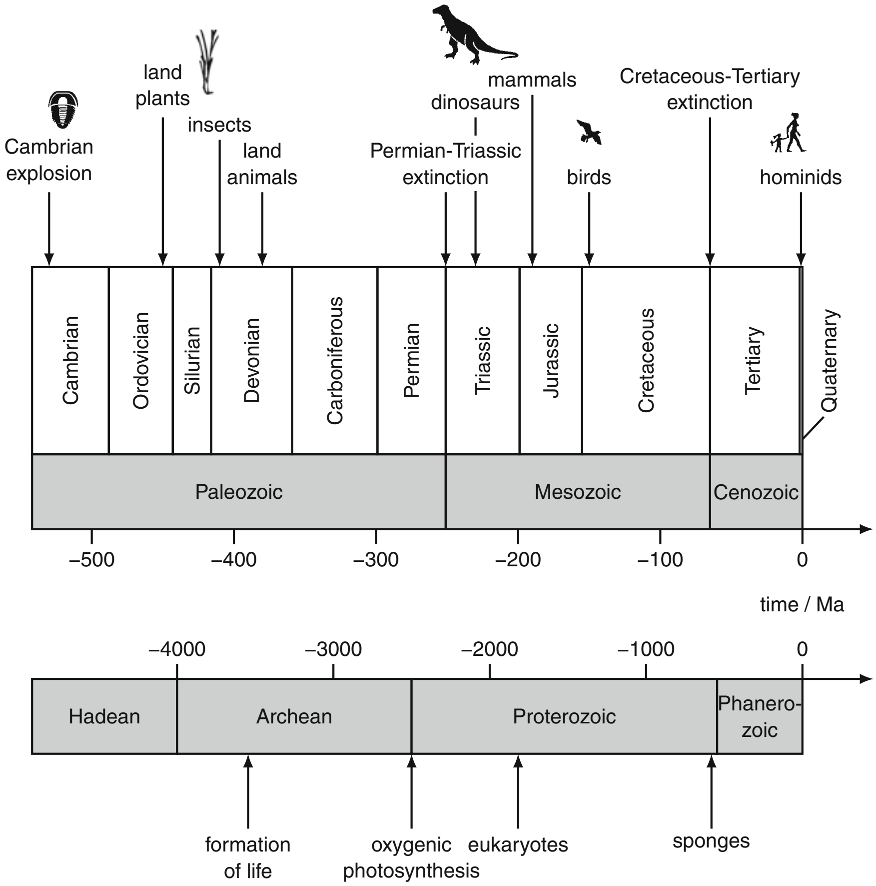


Fig. 2.12 Divisions of geologic time and major stations during development of life on Earth

energy from photosynthesis, started to occupy terrestrial habitats some 450 Ma ago (Smil 2002). These species dramatically intensified the overall production of oxygen and the transfer of carbon from the atmosphere to soils and sediments. Land animals followed during the Devonian and the Permian already saw a rich diversity of terrestrial life. Many species died out during the severe Permian-Triassic (250 Ma ago) and the Cretacious-Tertiary (65 Ma ago) extinction events but life resisted these dramatic incidents – which might have been caused by climatic changes, enhanced volcanic activity or impacts of huge meteorites – and recovered relatively quickly. Mammals that appeared 195 Ma before present eventually evolved hominids around 20 Ma ago (Smil 2002). These great apes are believed to be the ancestors of the species *homosapiens*, the modern humans which appeared in Africa about 200 000 years ago and subsequently spread to other continents.

2.2.5 Civilization

Modern civilization arose during the *Neolithic revolution* when early societies transformed from hunting and gathering to agriculture and settlement in villages and towns. Foraging societies with population densities of up to only a few humans per km^2 could not evolve functional specialization and social stratification (Smil 1994). Plant and animal domestication in agriculture allowed for enhanced and more reliable food production. Agricultural techniques ranging from burning or clearing the natural vegetation through the use of irrigation, fertilization and draft animals to the development of cropping cycles were invented in several regions of the world with Mesopotamia and Egypt being among the first centers of the emerging civilization.

Intensification of agriculture and food production was achieved through partial replacement of human labor by work done by animals, e.g. oxen, buffaloes, and horses, used for plowing. Since biomass growth through photosynthesis is directly linked to the availability of water (cf. Sects. 3.4 and 4.3) with one kilogram of important crops typically requiring up to 1000 kg water, irrigation is essential in many regions. Gravity-driven irrigation using canals or dams has a relatively low energy demand, but in many cases it was necessary to lift water over considerable heights by human or animal power, often assisted by mechanical devices. Finally, cropping led to deficits in nutrients – especially of nitrogen – and thus ways to recycle these indispensable materials had to be developed.

Once sufficiently advanced agricultural techniques had been developed, higher population densities that ultimately led to the formation of more complex societies living in cities became possible. Building the *great pyramid* of Giza, with a mass of over 6 Mt which was completed within 20 years around 2550 BCE (Before the Common Era), required planning, logistics, supervision of tens of thousands of workers, and technical skills, all on very high levels. It is interesting to note that the world population at that time of these admirable achievements is believed to have been less than 20 million (Fig. 2.13).

Before the advent of the industrialized civilization driven by fossil fuels, the energy required for agricultural needs and the erection of buildings was obtained through human and animal labor, kinetic energy of water and wind, as well as chemical energy stored in biomass. Humans can only deliver mechanical power on the order of 100–200 W over longer periods of time, whereas a horse (1 horsepower $= 735$ W) is much stronger. On the other hand, the Roman watermill complex located at Barbegal in Southern France was already able to deliver some 30 kW (Smil 1994). Since energy supply was limited and yields from agricultural production remained relatively constant, the world population did not strongly increase from the time of the early Roman Empire (400×10^6 at the beginning of the common era) until the 17th century (545×10^6 in 1650).

England was the first country to employ coal as an additional energy source on large scale. By 1650, the coal production had already amounted to more than 2 Mt (Smil 1994). Coal replaced wood in household heating, was used as reducing agent in steel production, and allowed for the invention of the steam engine, a machine able to

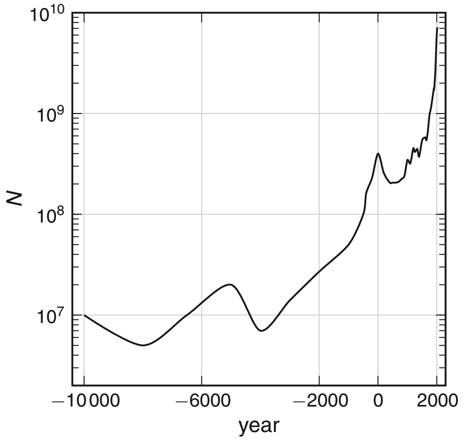


Fig. 2.13 Upper estimates of historical world population between 10 000 BCE and 2014, data from US Census Bureau

transform the chemical energy in coal into mechanical energy. Around 1800, steam engines outperformed both watermills and windmills and could also be employed to drive large ships and locomotives (see Fig. 2.14). When the first oil fields were detected after 1850, a convenient liquid fuel with high energy content became available. These liquid hydrocarbons are highly suitable to drive internal combustion engines which became available before 1900 and are the basis for transportation in automobiles and airplanes. At about the same time, steam turbine rotating generators for the production of electrical energy were developed and quickly utilized for lighting, electric railroads, and the beginning of the telecommunications industry.

Another fundamental breakthrough was related to the development of fertilizers. Phosphates became available from treatment of phosphate rocks with sulfuric acid, while progress in mining resulted in the discovery of potassium carbonate

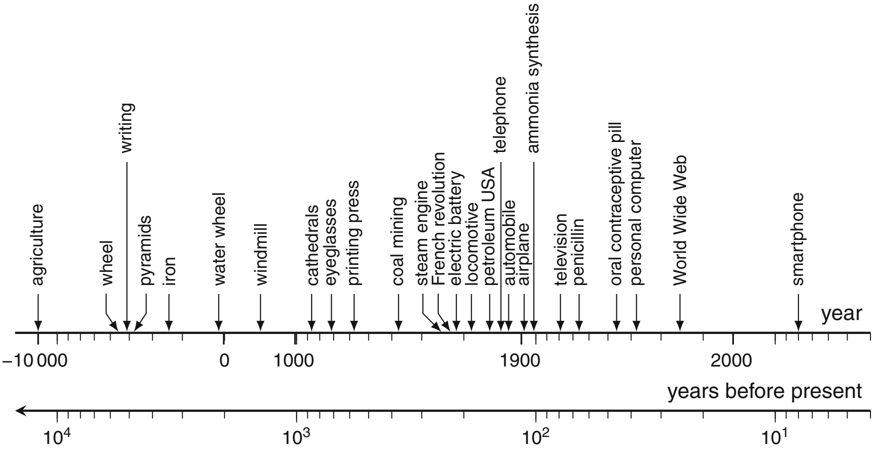


Fig. 2.14 Chronology of selected achievements during development of human civilization, from Smil (1994) and other sources (present = 2015, *right* end of *upper* axis: 2011, *lower* axis: 4)

and chloride deposits. The supply of nitrogen was improved by nitrate deposits, ammonia recovered from coke ovens or synthetically manufactured in the cyanamide process and the later developed, much more energy-efficient Haber–Bosch process (see Sect. 4.4). These artificial fertilizers and progress in the development of chemicals for protecting crops made it possible to nourish a strongly expanding world population that had reached its first billion shortly before the year 1800 and is expected to reach 7.5 billion by 2018 (Box 2.1 and Fig. 2.15).

Box 2.1 Expected Development of the World Population

Data for the development of the world population since 1950 as well as the predicted future numbers up to 2050 are shown in Fig. 2.15. Mathematically, the development of the number of individuals N with time t can be approximated by (Eq. (2.5)),

$$\frac{\mathrm{d}N}{\mathrm{d}t} = k(t)N \tag{2.5}$$

where k is the growth rate of the population that can be calculated with the birth rate b and the death rate d according to (Eq. (2.6)).

$$k(t) = \frac{b(t) - d(t)}{N(t)} \tag{2.6}$$

Early attempts to describe the population dynamics by Malthus assumed a constant growth rate and predicted an exponential increase of the number of individuals (Eq. (2.7)).

$$N(t) = N_0 \mathrm{e}^{k(t-t_0)} \tag{2.7}$$

Figure 2.15 reveals that this is unrealistic as the actual growth rate has been decreasing from around 2 % a^{-1} in 1970 to less than 1.2 % a^{-1} after 2000 and is expected to decline further. A more realistic growth model according to Verhulst assumes a limited growth until a capacity K has been reached and results in the following development of growth rate and number of individuals as a function of time (Eqs. (2.8) and (2.9)).

$$k(t) = k_0 \left(1 - \frac{N(t)}{K}\right) \tag{2.8}$$

$$N(t) = \frac{K N_0 \mathrm{e}^{k_0(t-t_0)}}{K + N_0(\mathrm{e}^{k_0(t-t_0)} - 1)} \tag{2.9}$$

The values calculated with a capacity of 11×10^9 cap depicted in Fig. 2.15 show a quite good agreement with the predicted development of the world population according to the US Census Bureau.

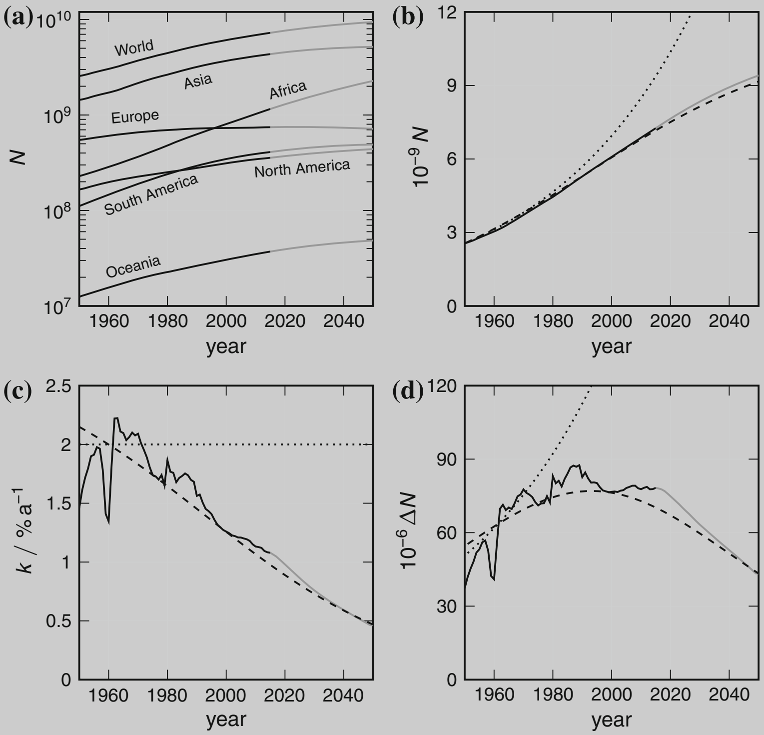


Fig. 2.15 **a** Development of regional and world population between 1950 and 2050, **b** world population, **c** world population growth rate, **d** annual population change, data from US Census Bureau, October 2015, *black lines*: data up to 2015, *gray lines*: projections for time after 2015, *dotted lines*: exponential growth (calculated with $k = 2\,\%\,a^{-1}$), *dashed lines*: logistic growth (calculated with $k_0 = 2.8\,\%\,a^{-1}$, $K = 11 \times 10^9$)

The United Nations attempt to assess the overall status of the development in different countries and the world through the Human Development Index (HDI, see Table 7.1) which takes into account (i) the life expectancy at birth, (ii) the overall education via the adult literacy rate and the gross enrollment ratio and (iii) the per-capita gross domestic product (GDP) as a measure of the standard of living. Figure 2.16 reveals that great inequalities in human development occur in different regions of the world.

In the 2014 report, 31 countries having a HDI value of more than 0.85 were listed with life expectancies close to or more than 80 a, very high literacy rates, and GDP values above 18 000 USD $cap^{-1}\,a^{-1}$. Figure 2.17 shows, as an example, that the life expectancy in Germany has more than doubled since 1875. The respective development of the average world data reveals that considerable progress has been achieved on the global scale. The least developed 33 countries with HDI values below 0.5 corresponding to life expectancies around 50 a, literacy rates of 30–70 %, and a

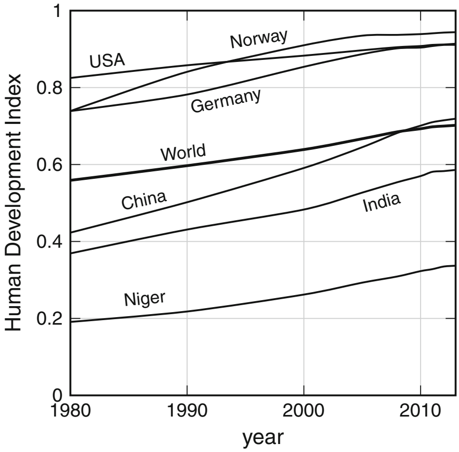


Fig. 2.16 Human Development Index trends for selected countries between 1980 and 2013, data from United Nations Development Programme

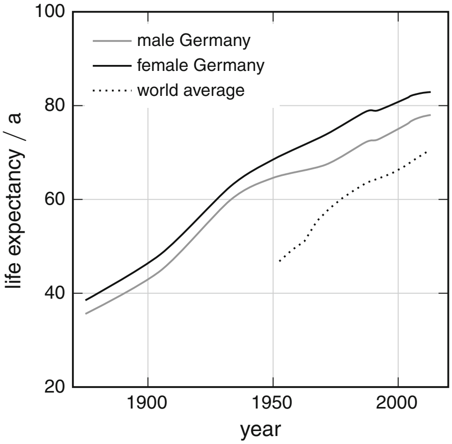


Fig. 2.17 Development of life expectancy at birth for Germany (male and female sexes, data from German Federal Statistical Office) and for the world (both sexes combined, data from United Nations, Department of Economic and Social Affairs)

GDP of no more than 1700 USD $cap^{-1}\,a^{-1}$ are mainly located in Africa. It will be of utmost importance to improve the conditions in these regions of the world. On the other hand, the relatively comfortable conditions in the developed countries are to a large extent based on the availability of moderately priced fossil fuels which are by far the most important drivers of industrialized economies. The limits for anthropogenic energy and material flows as well as the implications for the future development of mankind will be discussed in Chaps. 6 and 7.

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Chapter 3
Energy Balance of the Earth

In this chapter the energy transformations on Earth are described. The surface temperature, which is a key variable for the climate, is on the one hand determined by the global energy balance between radiative energy coming from the Sun and radiative energy emitted back to space by the Earth (Fig. 3.1a). On the other hand, the atmosphere has a strong impact on the global energy balance as it efficiently absorbs infrared radiation coming from the surface of the Earth. As a consequence, the surface temperature is much higher than it would be without the atmosphere.

The basis for life on Earth is the ability to convert energy received from the Sun into energy-containing chemical components via *photosynthesis*. The Earth's biosphere has been evolving over long periods of time and is capable of changing energy-relevant properties of the Earth and altering the energy balance on a global scale.

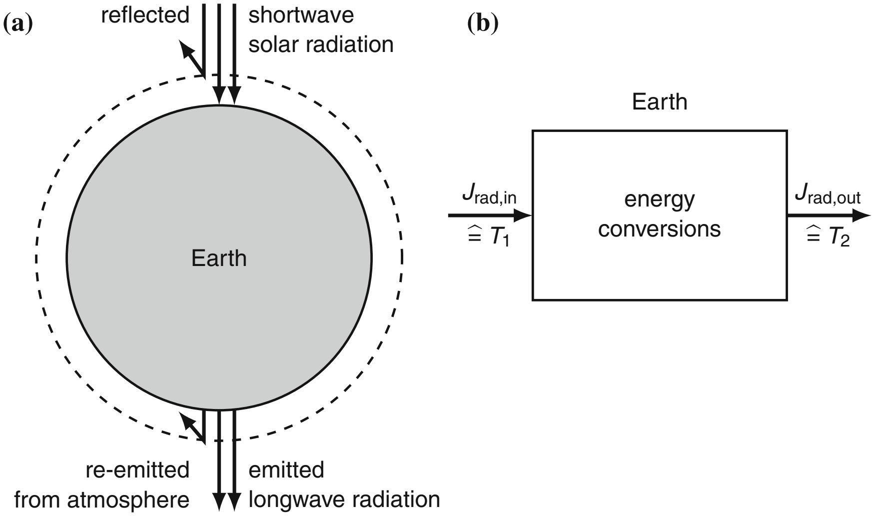

Fig. 3.1 Energy transformations on Earth

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DOI 10.1007/978-3-319-29495-7_3

From an engineering point of view, the Earth is an energy converter like the technical converters described in the subsequent chapters of this book (Fig. 3.1b). Shortwave radiation from the Sun is transformed into longwave radiation that is re-emitted by Earth, but also into latent heat contained in the atmosphere and the ocean, as well as into mechanical energy in wind, rivers, and ocean currents. The complexity of the Earth system is tremendous and a full understanding of the processes taking place in it has not yet been achieved. However, several general properties, limiting cases, and typical phenomena occurring within the Earth system can be derived from relatively simple energetic analyses.

3.1 Energy Exchange by Radiation

The amount of energy per unit area and wavelength λ that is emitted by a black body at temperature T can be described with Planck's law of radiation (Eq. (3.1)):

$$\varepsilon(\lambda, T) = \frac{2\,h\,c^2}{\lambda^5}\frac{1}{\mathrm{e}^{\frac{h\,c}{\lambda\,k\,T}} - 1}. \tag{3.1}$$

Here, h is Planck's constant ($6.626 \times 10^{34}\,\mathrm{J\,s}$), c the speed of light in a vacuum ($2.998 \times 10^8\,\mathrm{m\,s^{-1}}$), and k the Boltzmann constant ($1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}$). The cor-

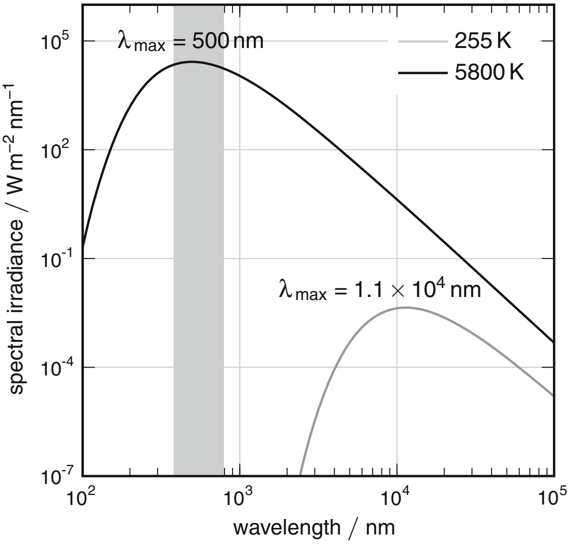


Fig. 3.2 Spectral radiance as a function of radiation wavelength for two black bodies (Sun with 5800 K and Earth with 255 K), *gray area* visible light

responding spectral irradiance ε for the Sun with a surface temperature of 5800 K and for the Earth with a temperature of 255 K at the top of the atmosphere is shown in Fig. 3.2.

Wien's displacement law (Eq. (3.2)) states that the shape of all black body spectra is similar and is only a function of temperature. As a consequence, the wavelength at which the intensity of the radiation from a black body is at a maximum can be described with:

$$\frac{\lambda_{\max}}{\mu\mathrm{m}} = \frac{hc}{4.9651\,kT} = \frac{2897.8}{T/\mathrm{K}}. \tag{3.2}$$

It can be seen in Fig. 3.2 that radiation from the Sun has a maximum in the visible region of light (500 nm) whereas the Earth emits predominantly in the infrared ($\lambda_{\max} = 11\,\mu\mathrm{m}$). Integrating the Planck equation (Eq. (3.1)) over all wavelengths yields the Stefan–Boltzmann law for the total flux density of a black body J_{rad}:

$$J_{\mathrm{rad}} = \int_0^\infty \varepsilon\,\mathrm{d}\lambda = \frac{2\,\pi^5 k^4}{15\,h^3 c^2}\,T^4 = \sigma\,T^4. \tag{3.3}$$

Here $\sigma = 5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$ is the Stefan–Boltzmann constant. According to Kirchhoff's law, the emissivity of a body equals its absorptivity at thermal equilibrium. For any real (*gray*) body not exhibiting the perfect blackbody properties, one thus obtains that the body absorbs and emits a reduced flux density

$$J_{\mathrm{rad}} = (1 - a)\,\sigma\,T^4 \tag{3.4}$$

with a the emissivity or *albedo* of the gray body.

Box 3.1: Calculation of the Earth Temperature at Top of the Atmosphere

At the mean distance of the Earth from the Sun, the solar flux density of radiative energy equals $1365\,\mathrm{W\,m^{-2}}$. As this value relates to the flat shadow area πr^2 of the spherical Earth with radius r, the flux density J_{solar} per total surface area $4\pi r^2$ of the Earth amounts to $341\,\mathrm{W\,m^{-2}}$.

Since the global average of the planetary albedo is $a = 0.3$, the following flux density is absorbed by the Earth:

$$J_{\mathrm{abs}} = (1 - a)\,J_{\mathrm{solar}} = 239\,\mathrm{W\,m^{-2}}. \tag{3.5}$$

For a more detailed assessment of the reflective properties of the Earth surface see Fig. 3.10. In thermal equilibrium one can now calculate the average radiation temperature at the top of the atmosphere or *effective* temperature T_{eff} of the Earth.

$$J_{\mathrm{abs}} = J_{\mathrm{em}} = \sigma\,T_{\mathrm{eff}}^4 \tag{3.6}$$

The resulting effective temperature at the outer atmosphere of 255 K (−18 °C) is much lower than the actual average global surface temperature of 288 K (+15 °C).

Even if the Earth were a black body with $a = 0$, the atmospheric temperature calculated with Eqs. (3.5) and (3.6) of 278 K (+5 °C) would be significantly lower than the actual surface temperature. This important difference can only be understood if the greenhouse effect is considered.

3.2 Role of the Atmosphere and Greenhouse Effect

Figure 3.3 shows that the radiative spectrum of the Sun at the top of the atmosphere is relatively similar to the calculated values for a black body with a surface temperature of $T = 5800$ K. The measured spectrum at sea level, however, reveals considerable differences. The irradiance at short wavelengths is lower than incoming from the Sun with radiation below ca. 300 nm not reaching the sea level at all. On the other hand, the spectrum in the region of higher wavelengths exhibits certain characteristic bands with decreased values.

The explanation for this complex behavior is found in the different transmission properties of the atmosphere for incoming solar and outgoing terrestrial radiation. While shortwave radiation from the Sun can transmit relatively unhindered, except for ultraviolet radiation, the atmosphere is much less transparent to infrared radiation

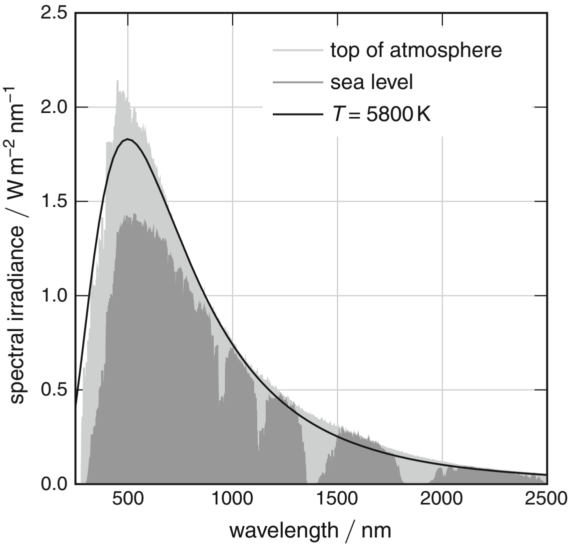


Fig. 3.3 Spectral radiance as a function of radiation wavelength at top of atmosphere and sea level (Gueymard 1995, 2001), *solid line* depicts black body radiation with $T = 5800$ K assuming a solid angle of 6.8×10^{-5} steradian for the solar disk

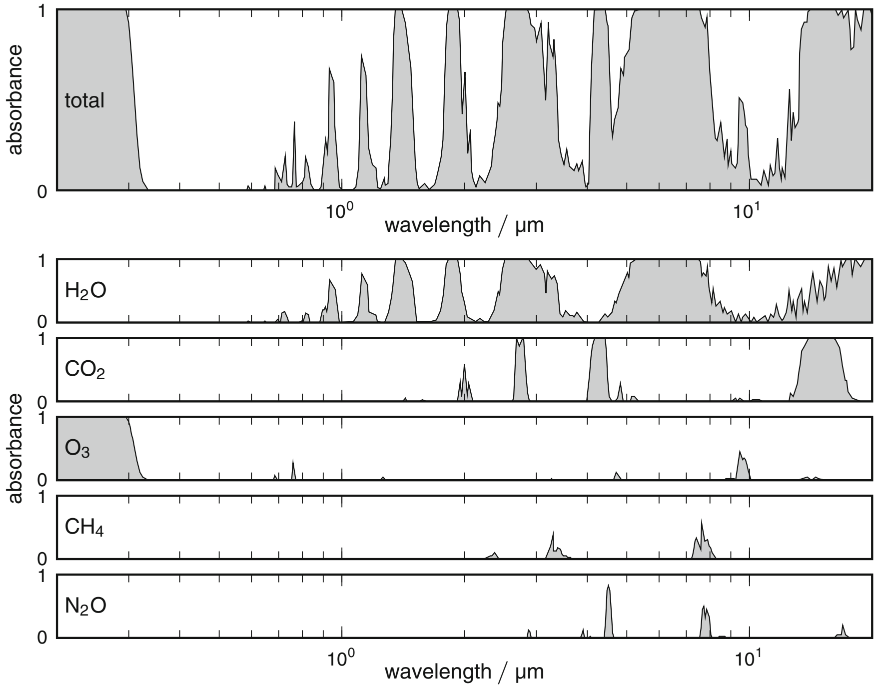


Fig. 3.4 Absorption as a function of wavelength by constituents of the atmosphere and by the atmosphere as a whole, data obtained with the spectral calculator of GATS, Inc. (http://www.spectralcalc.com, Gordley et al. 1994)

emitted from the Earth's surface. Figure 3.4 shows that especially water vapor and carbon dioxide, but also other trace gases such as methane and nitrous oxide, are able to absorb infrared radiation quite strongly.

The ability of atmospheric constituents to interact with radiation emitted from Earth's surface changes the global radiative energy balance considerably. A very simple model illustrating this fact has been presented by Hartmann (1994). It considers the atmosphere to be a single layer which is a blackbody for terrestrial (infrared) radiation while being completely transparent for incoming (shortwave) radiation from the Sun. Figure 3.5 reveals that the energy balance at the top of the atmosphere is the same that was originally obtained (Eq. (3.6)) while the surface of the Earth now emits twice the radiative power than the outer atmosphere obtains by solar heating (Eq. (3.7)).

$$J_\mathrm{s} = 2\,(1 - a)\,J_\mathrm{solar} = \sigma\,T_\mathrm{s}^4 \tag{3.7}$$

As a result, an average surface temperature of 303 K (30 °C), which is 48 K higher than at the top of the atmosphere, would be obtained. This warming impact of the atmosphere is called *greenhouse effect*. Even higher surface temperatures are obtained if the atmosphere is assumed to consist of multiple layers each being transparent for shortwave solar radiation, but impermeable for longwave infrared radia-

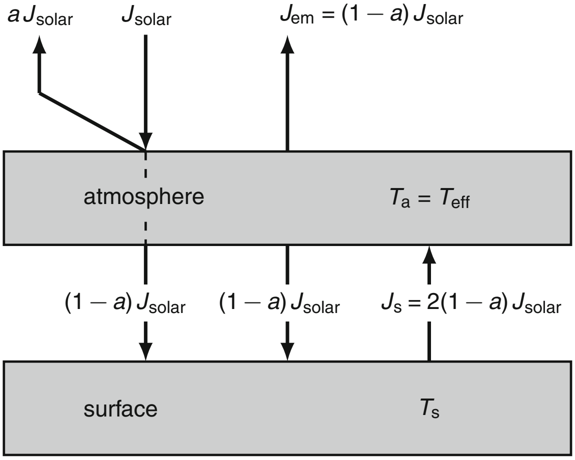


Fig. 3.5 Simple atmospheric model with single atmospheric layer emitting the same radiation to space and the surface

tion. In that case, one can easily show that the outer atmospheric layer remains at the effective temperature (cf. Box 3.1) while the lower layers become increasingly warmer with the surface temperature reaching

$$T_s = (n+1)^{0.25}\,T_{eff} \tag{3.8}$$

where n is the number of atmospheric layers. With such a model, even extreme surface temperatures such as those occurring on Venus (cf. Table 2.1) can be qualitatively explained.

For Earth, the actual greenhouse effect is lower than calculated with the single-layer model depicted in Fig. 3.5 because Earth's atmosphere is partially transparent to infrared radiation. This is especially true in the spectral range between 8 and 14 µm. Here an *atmospheric window* exists where around 30 % of the surface radiation passes unabsorbed and reaches space. To take this phenomenon into account, a *leaky* greenhouse model has been presented (Jacobs 1999). Figure 3.6 shows a single atmospheric layer that is partially transparent for the longwave radiation coming from Earth's surface. If one assumes that the atmosphere absorbs a factor f of the surface radiation, the energy balances for the surface and the atmosphere result in the following equations:

$$T_s = \left(\frac{2}{2-f}\right)^{0.25} T_{eff} \tag{3.9}$$

$$T_a = \left(\frac{1}{2-f}\right)^{0.25} T_{eff} \tag{3.10}$$

The observed surface temperature of Earth (288 K) would correspond to an atmospheric absorptivity of $f = 0.77$ and an atmospheric model temperature of 242 K.

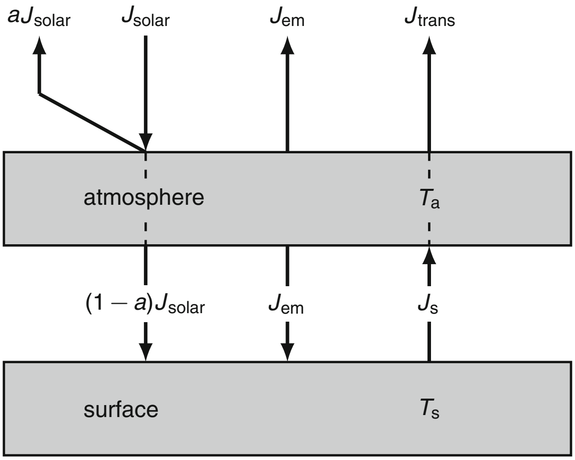


Fig. 3.6 Simple atmospheric model with atmospheric layer partially transparent for infrared radiation

A realistic assessment of all contributions of radiative and non-radiative processes to the energy balance of the surface and the atmosphere is shown schematically in Fig. 3.7. The Earth absorbs 70 % of the incoming solar radiation (341 W m^{-2}) and reflects 30 %. Almost 50 % of the radiation at the top of the atmosphere reaches the surface and is absorbed (161 W m^{-2}). The surface obtains an additional 333 W m^{-2} as longwave radiation from the atmosphere and emits itself 396 W m^{-2} as radiation and an additional 97 W m^{-2} caused by convection and evapotranspiration. The atmosphere emits 199 W m^{-2} to space while 40 W m^{-2} passes directly from the surface through the atmospheric window. It is evident that neither the heat flux received from the inner Earth nor the anthropogenic contribution – mainly caused by burning of fossil fuels – have a noticeable direct effect on the global energy balance. Their values are based on the anthropogenic energy flow from Fig. 5.10 (2014: 1.7×10^{13} W) and a conductive heat flow estimate, respectively, assuming a geothermal gradient of 0.03 K m^{-1} and a thermal conductivity in the Earth's crust of 2 W m^{-1} K^{-1}.

Given the actual flux density emitted from Earth's surface (396 W m^{-2}) one can calculate an average surface temperature of 289 K (16 °C). The real greenhouse effect is thus only 34 K or 70 % of the maximum value calculated with the simple model described in Fig. 3.5. Estimated values for the contribution of individual atmospheric constituents are summarized in Table 3.1. It can be seen that water vapor is by far the most important greenhouse gas. However, the three trace gases that are strongly influenced by human activities (CO_2, CH_4, and N_2O) account for around one third of the overall greenhouse effect according to these calculations. Although the atmospheric methane and nitrous oxide concentrations are very low, their relative contribution is significant due to the high global warming potential relative to carbon dioxide. Thus it is understandable that a drastic increase in the atmospheric concentrations of these three components may give rise to an additional anthropogenic greenhouse effect of several K.

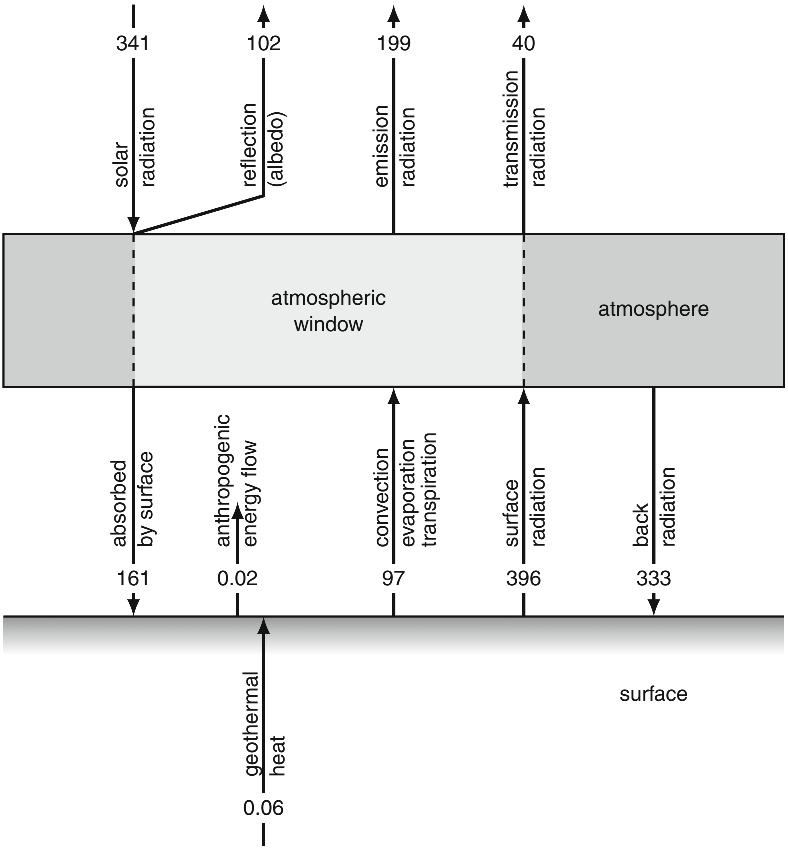


Fig. 3.7 The Earth's annual global mean energy budget (numbers in W m^{-2}) according to Kiehl and Trenberth (1997), Trenberth et al. (2009) with additional values for anthropogenic and geothermal energy flows

A concept for assessing the influence of anthropogenic activities (e.g. the emissions of greenhouse gases) on the global radiation budget is *radiative forcing RF*, which is defined as the change in net irradiance at the tropopause (i.e. at 15 km height) after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state that is maintained at the unperturbed values (IPCC 2007a). The global average temperature at the surface is approximately linearly dependent on radiative forcing (Eq. (3.11)),

$$\Delta T_s = \gamma\, RF \tag{3.11}$$

Table 3.1 Contribution of individual gaseous components to the total greenhouse effect, example values for historical situation in 1984 (Kondratyev and Moskalenko 1984; IPCC 2007a)

Gas	1984 concentration ppm	Global warming potential[a]	Warming effect[b] K
H_2O	~4000		20.6
CO_2	340	1	7.2
O_3	0.04		2.4
N_2O	0.30	298	1.4
CH_4	1.62	25	0.8
Others			0.8
Total			33.2

[a] Radiative forcing, relative to carbon dioxide, of greenhouse gas in present-day atmosphere integrated over time horizon of 100 a

[b] Values in good agreement with *clear sky* data given in Kiehl and Trenberth (1997)

where γ is the climate sensitivity parameter with a typical value of $0.8\,\mathrm{K\,m^2\,W^{-1}}$ obtained from the generally expected temperature rise of 3 K for doubling of the carbon dioxide concentration relative to the pre-industrial level (Knutti and Hegerl 2008).

3.3 Spatio-Temporal Variations

The global energy balance is the integral picture of a locally and temporally differing situation on Earth. Caused by the movement of Earth around the Sun (Fig. 3.8) and its rotation, the solar flux density at the top of the atmosphere is dependent on latitude, season, and time of the day.

The calculated average daily insolation as a function of latitude and day of the year is depicted in Fig. 3.9. The gray areas show that poleward latitudes remain in complete darkness for up to 6 months per year. As Earth's orbit is not exactly circular, the maximum solar flux density in the Southern Hemisphere is at present slightly higher than in the Northern Hemisphere. Interestingly, the insolation at high latitudes at summer solstice is higher than at the equator. This is caused by the very long summer days whereas the days at the equator have a constant duration of 12 h.

Globally, about 30 % of the radiation at the top of the atmosphere is reflected by the atmosphere, clouds, and Earth's surface. However, the albedo has a strong geographic distribution (Fig. 3.10). High values occur in the polar regions with large snow-covered areas and solar zenith angles. On the other hand, the ocean surface has a very low albedo, the value of which can reach less than 10 % in areas that are lowly covered with clouds.

As a result of the incoming solar radiation as well as the atmospheric and surface conditions, the radiative flux density at Earth's surface exhibits spatio-temporal variations. Figure 3.11 shows the measured annual average values over the time period between 1983 and 2005. Areas close to the equator receive up to $290\,\mathrm{W\,m^{-2}}$ on

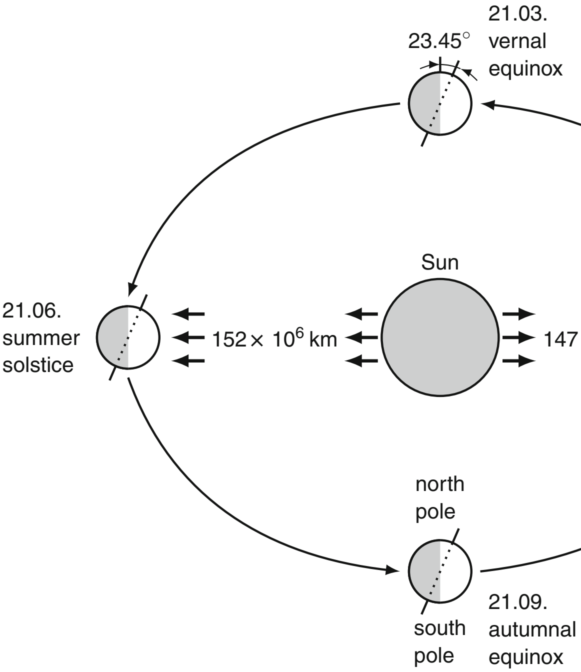
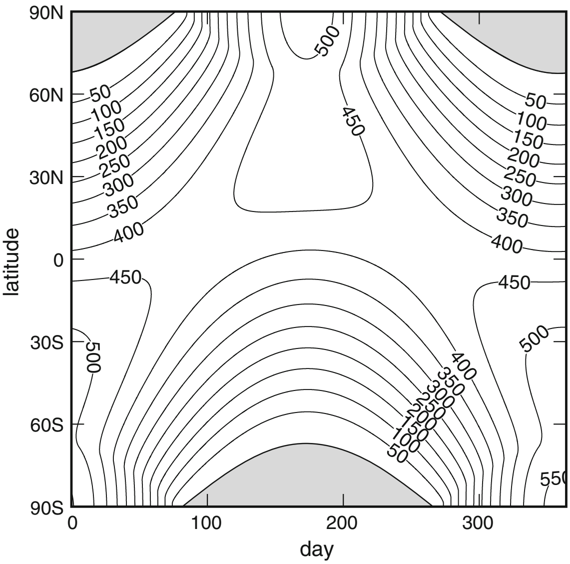


Fig. 3.8 Earth's orbit around the Sun and seasons in the Northern Hemisphere

Fig. 3.9 Contour map of the average daily radiance in W m^{-2} at the top of the atmosphere as a function of latitude and day of year, calculated according to Hartmann (1994)



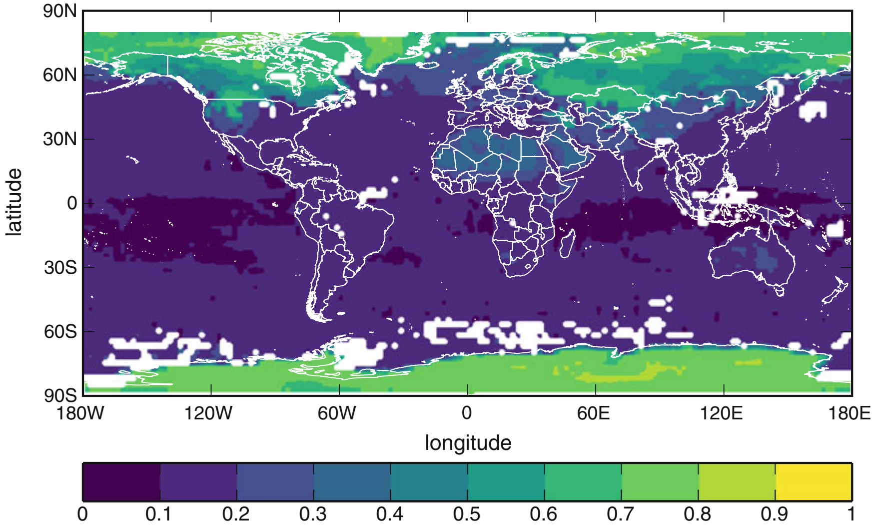


Fig. 3.10 Average Earth albedo for February 1989, 1° spatial resolution (latitude/longitude), Barkstrom (1984, 2009), *white areas* no data

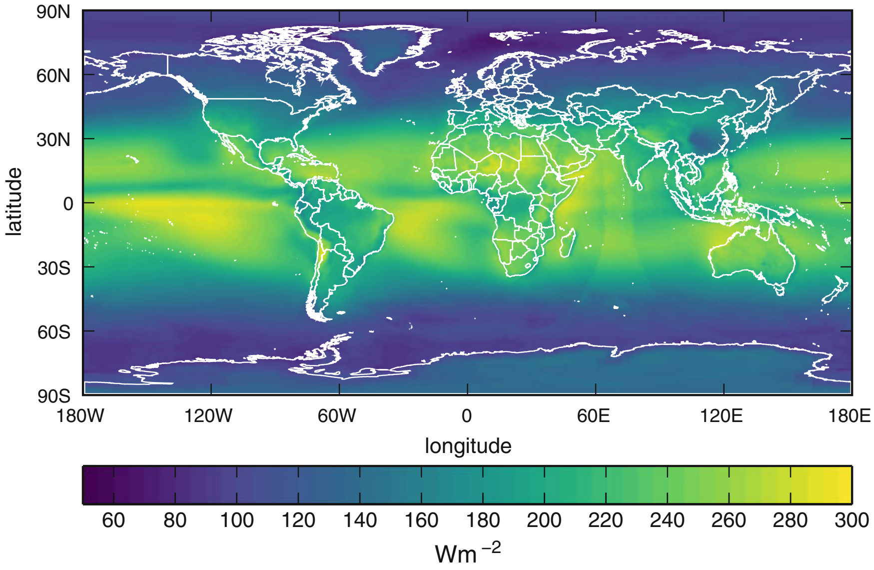


Fig. 3.11 Annual average insolation on horizontal Earth surface over 22 years (July 1983–June 2005), data obtained from NASA Langley Research Center, Atmospheric Science Data Center, http://eosweb.larc.nasa.gov/sse/, 1° spatial resolution (latitude/longitude)

average while some parts of the polar north have annual insolations of significantly less than 100 W m^{-2}.

The surface temperature on Earth is not only dependent on the radiative flux density and the surface properties. It also has to be taken into account that the energy transfer from the surface to the atmosphere by convective heat transport and evapotranspiration is regionally different. Moreover, there are flows of energy in the lateral direction transported by the atmosphere and the ocean. The resulting spatial distribution of the annual average surface temperature for the time period 1961–1990 is depicted in Fig. 3.12. The values differ between −59 °C in the Antarctic and +29 °C in tropical regions with a global mean temperature of +15 °C.

The conditions at selected locations on Earth are summarized in Table 3.2. One can see that the annual average temperatures in large regions of the Earth, approximately ranging from the south of Australia and the south of Canada, are between the freezing point of water and almost 30 °C. Only in less habitable areas close to the poles do the temperatures decrease dramatically. This is only to a minor extent caused by the flux density of the solar irradiation. The very large albedo has a much stronger effect in these snow-covered regions. A very simple energy balance model allowing for approximation of this global temperature distribution will be presented in Sect. 3.5.1.

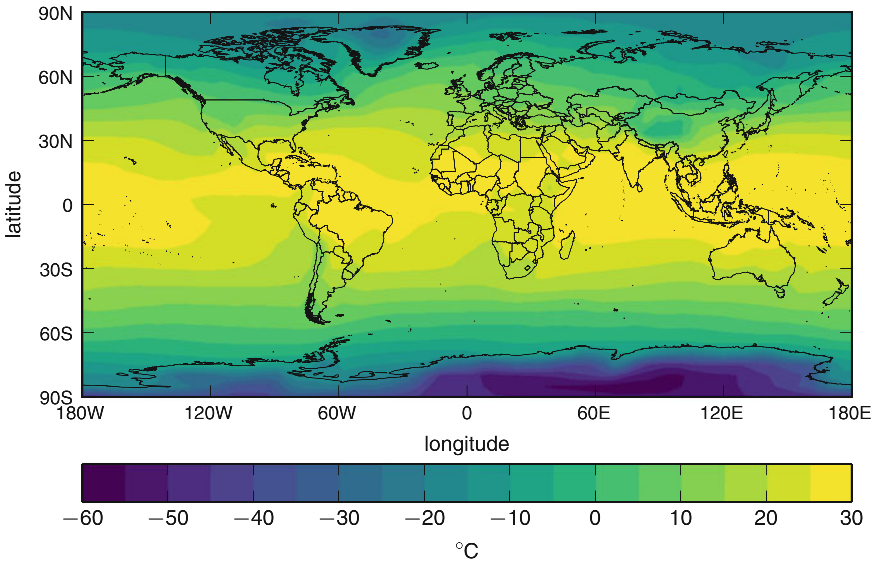


Fig. 3.12 Annual average Earth surface temperature for time period 1961–1990, data from the UK Met Office Hadley Centre, http://www.cru.uea.ac.uk/cru/data/temperature/, 5° spatial resolution (latitude/longitude)

Table 3.2 Selected examples of conditions on Earth

	Position		Surface irradiance[a]	Albedo[b]	Average temperature[c]
	Latitude	Longitude	$W\,m^{-2}$		°C
Murmansk, Russia	69N	34E	130.8	0.6010[d]	−21.7
Vancouver, Canada	49N	123W	154.2	0.1695	−1.0
Karlsruhe, Germany	49N	8E	139.2	0.2109	+9.4
Los Angeles, USA	34N	118W	173.8	0.1764	+20.8
Shanghai, China	31N	121E	202.9	0.1417	+17.1
Dubai, UAE	25N	55E	240.4	0.2587	+25.7
Hawaii, USA	21N	158W	248.3	0.1098	+27.4
Mumbai, India	19N	73E	247.1	0.1245	+27.4
Lagos, Nigeria	6N	3E	200.0	0.1273	+25.4
Singapore	1N	104E	252.9	0.1091	+25.2
Rio de Janeiro, Brazil	23S	43W	185.8	0.1323	+23.6
Sydney, Australia	34S	151E	185.4	0.1273	+19.7
Vostok, Antarctic	78S	107E	140.8	0.7930[d]	−56.1

[a] Average values for 1983–2005, see Fig. 3.11

[b] Average values for 1989 except for Murmansk and Vostok, data source see Fig. 3.10

[c] Average values for 1961–1990, see Fig. 3.12

[d] Values for February 1989

3.4 Photosynthesis

Photosynthesis means a photo-biological reaction that converts CO_2 and water (and other minor components) by addition of solar radiative energy input into the organic molecules which constitute living organisms. It thereby connects an energy flow (solar radiation) and a material flow (reducing carbon in its oxidized form into reduced forms in organic molecules). The reaction is highly endothermic and thus represents an energy conversion process that converts radiative energy into chemical energy. The chemical energy stored in photosynthetic autotrophic organisms (plants, algae, *biomass*) provides the energy for all other forms of life in the biosphere. In technical combustion systems, the chemical energy stored in biomass (and in fossil fuels derived over geological time scales) can be converted into heat and also further into other forms of energy, if desired. Biomass also provides a wide variety of materials that are useful in man's daily life.

The main constituents of biomass formed by photosynthesis or related metabolic reactions include carbohydrates (sugars, starch, lignocellulose), lipids (fatty acid esters), hydrocarbons (terpenes) and other complex biopolymer molecules (proteins, steroids, DNA etc., Larcher 2003; Schlesinger 1997). Lignocellulose is by far the most abundant kind of biomass on Earth as it constitutes the major part of terrestrial plants where it is responsible for mechanical stability.

The overall reaction for photosynthesis as it leads to glucose as a carbohydrate molecule is given in React. (3.12), which represents a process that occurs in two stages. First, the capture of light energy by chlorophyll molecules allows water molecules to be split and high-energy molecules to be formed. This reaction is followed by carbon reduction, in which CO_2 is converted to carbohydrates.

$$6\,CO_2 + 6\,H_2O \longrightarrow C_6H_{12}O_6 + 6\,O_2, \qquad \Delta_R H = +2876.4\,\mathrm{kJ\,mol^{-1}} \tag{3.12}$$

In terrestrial plants, CO_2 reacts from the gas phase, whereas water in general enters the plant in liquid form via the plant roots. In addition to the stoichiometric H_2O consumption via the photosynthesis reaction, large amounts of water are required for evapotranspiration (for temperature control), as well as for transporting nutrients in dissolved form into the plant. In aquatic plants, CO_2 enters the organism dissolved in water. Here, the lignocellulosic biomass material is not needed for mechanical stabilization and therefore is not formed.

Integral Photosynthesis Yield and Energy Efficiency

Achievable yields of plants and crops have been important since the times when humans started to cultivate plants to generate food on purpose. Limited farmland availability to feed human communities and later the rules of economy have forced farmers to think of efficiency when growing food crops. The amount of biomass produced by photosynthesis during a defined period of time (e.g. the growing season) is limited by the complex metabolic mechanisms in the particular plant species and, in addition, by a number of external factors: quality of the soil and time-histories of sunshine, temperature, available water (precipitation), i.e. climate conditions, as well as extraordinary weather events (flooding, storms, hail, etc.).

As a quantitative measure, the yield of dry matter production of a plant community is called net primary production (*NPP*) and is expressed as mass of dry organic matter per ground area and year (Eq. (3.13))

$$NPP = \int_{\mathrm{time}} r_{\mathrm{photosynthesis}}(PPFD, T, c_{H_2O}, \ldots) \tag{3.13}$$

with *NPP* in $\mathrm{kg\,m^{-2}a^{-1}}$ or $\mathrm{t\,ha^{-1}a^{-1}}$ and *PPFD* the photosynthetic photon flux density. High net primary production is limited to those regions of the continents and the ocean that offer plants a favorable combination of water, temperature, and nutrient availability (Larcher 2003, pp. 165–168). In terrestrial systems, these regions are found in the humid tropics and in fresh water systems, in the zone between 40 to 60N and 40 to 60S latitude. The most productive plant communities are found in belts where land and water meet, i.e. in shallow waters near the coasts and coral reefs, in swamps, and swamp forests in warm climates (Table 3.3). Corresponding amounts of phytomass are 40–80 $\mathrm{kg\,m^{-2}}$ in tropical rain forest, 10–50 $\mathrm{kg\,m^{-2}}$ for tidal zones and temperate forest, 2–5 $\mathrm{kg\,m^{-2}}$ in meadows and steppe, and less than 0.1 $\mathrm{kg\,m^{-2}}$ in the open ocean. A large proportion of the Earth surface, both on land

and on water, permits only moderate *NPP*. On 41 % of the terrestrial surface, water is the most growth-limiting environmental factor, and on 8 % of the terrestrial surface, unfavorable temperatures are responsible for lower *NPP* (short growing seasons due to cold temperatures). In the tropical ocean it is nutrient deficiency, and in seas near the poles it is inadequate light that limits productivity.

The energy flow densities given in Table 3.3 can be used to calculate conversion efficiencies for the conversion of solar radiation energy into chemical energy. Resulting values when using lower heat of combustion *LHV* as biomass energy content (see Sect. 5.5) are in the order of 1 %. The natural process of photosynthesis is not optimized with respect to energy utilization but according to other criteria (e.g. stability of reproduction and response capability against external stress factors).

Individual plant species exhibit different values of *NPP*, examples of maximal dry matter yields are listed in Table 3.4 (with usable portion, i.e. *harvest index*, reaching

Table 3.3 Annual net primary production and energy flow density of different biomes of the Earth (after Larcher 2003, p. 166, based on various sources)

Type of vegetation	Area	Net primary production			
		Range	Mean		Range
	$10^6\,\mathrm{km}^2$	$\mathrm{kg\,m^{-2}a^{-1}}$	$\mathrm{kg\,m^{-2}a^{-1}}$	$\mathrm{Gt\,a^{-1}}$	$\mathrm{W\,m^{-2}}$[a]
Continents	149.0		0.78	117.5	0.39[b]
Tropical rainforest	17.0	1–3.5	2.2	37.5	0.5–1.8
Deciduous woodland (semiarid)	7.5	1.6–2.5	1.6	12.0	0.8–1.3
Deciduous forests (temperate)	7.0	0.4–2.5	1.2	8.4	0.2–1.3
Evergreen forests (temperate)	5.0	1–2.5	1.3	6.5	0.5–1.3
Boreal forests	12.0	0.2–1.5	0.8	9.6	0.1–0.8
Dry scrub and sclerophyllis	8.5	0.3–1.5	0.7	6.0	0.2–0.8
Savannas	15.0	0.2–2	0.9	13.5	0.1–1.0
Meadows and steppes	9.0	0.2–1.5	0.6	5.4	0.1–0.8
Tundra	8.0	0.01–0.4	0.14	1.1	0.005–0.2
Shrub deserts	18.0	0.01–0.3	0.9	1.6	0.005–0.2
Dry and cold deserts	24.0	0–0.01	0.003	0.07	0–0.005
Agricultural crops	14.0	0.1–4	0.65	9.1	0.05–2.0
Swamps, marshes	2.0	1–6	0.3	6.0	0.5–3.0
Inland waters	2.0	0.1–1.5	0.4	0.8	0.05–0.8
Ocean	361.0		0.155	55.0	0.08[b]
Open ocean	332.0	0.002–0.4	0.125	41.5	0.001–0.2
Upwelling zones	0.4	0.4–1	0.5	0.2	0.2–0.5
Coastal zones	26.6	0.2–0.6	0.36	9.6	0.1–0.3
Reefs and tidal zones	0.6	0.5–4	2.5	1.6	0.3–2.0
Brackish water	1.4	0.2–4	1.5	2.1	0.1–2.0
Global total (Earth)	510		0.336	172.5	0.17[b]

[a] With $LHV = 16\,\mathrm{MJ\,kg^{-1}}$

[b] Average value

Table 3.4 Maximal dry matter production (*NPP*) of different crop plants (selected examples from Larcher 2003, p. 164, based on various sources)

	Maximal yields $\text{kg m}^{-2}\text{ a}^{-1}$		Maximal yields $\text{kg m}^{-2}\text{ a}^{-1}$
C_4 grasses		Forest plants	
Sugar cane	6–8	Cypress	5.3
Maize (subtropic and tropic)	3–4	European black pine	2.5
Maize (temperate zones)	2–4	European beech	1.3
C_3 grasses		Intensive short rotation forestry	
Rice	2–5	Willow	5
Wheat	1–3	Poplar (hybrid)	3.5–4
Swamp grasses	5–10	CAM[a] plants	
Legumes		Opuntia[b]	4.5–5
Lucerne	3	Pineapple plantation	2–3
Soybeans	1–3	Cacti (natural habitat)	0.8–1.7
Root crops		Aquatic plants	
Manioc	3–4	Water hyacinth	1.5–20
Sugar beet	2–3	Seaweeds	3–5.5
Vegetable oil crop			
Oil palm[c]	2–4		

[a] Crassulacean acid metabolism
[b] With fertilization and daily irrigation
[c] Also higher values (up to $8\text{ kg m}^{-2}\text{ a}^{-1}$)

30–60 % for seed, 85 % for forage, and 50–70 % for timber production). With plant breeding and intensive cultivation methods, higher yields can be achieved than with natural plant communities in a given region. For example, for land plants (including trees), the annual biomass production can be increased to twice the normal value by irrigation and fertilization at levels adjusted to the requirements of each growth stage. At a global scale, average agricultural yields still remain far below maximum values, mainly due to less intensive use of the land and the low-quality crop varieties used.

Quantitative correlations between net primary photosynthetic production and external factors have been developed based on empirical data. For example, Lieth (1975, pp. 237–265) presented a simple regression analysis for large-area average productivity as affected by mean annual temperature and annual precipitation. Equations (3.14) and (3.15) give two separate nonlinear correlations based on 52 data sets in various climate zones and biomes. Figure 3.13 shows the resulting curves for dry matter and organic carbon production, assuming an average carbon content of 48.4 wt% is produced in the biomass.

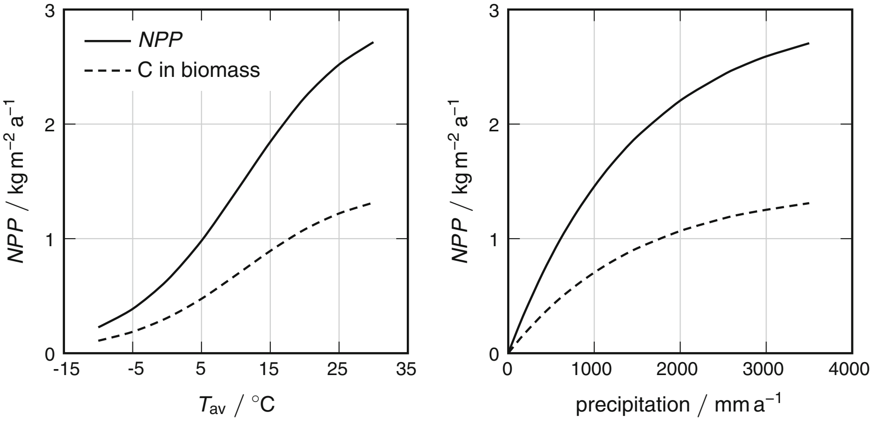


Fig. 3.13 Annual net primary production (*NPP*) as large-area average productivity, correlated with mean annual temperature T_{av} (*left*) and annual precipitation (*right*), based on 52 data sets (different regions, locations (Lieth 1975), carbon weight fraction in dry biomass: 0.484, equivalent to $CH_{1.6}O_{0.7}$)

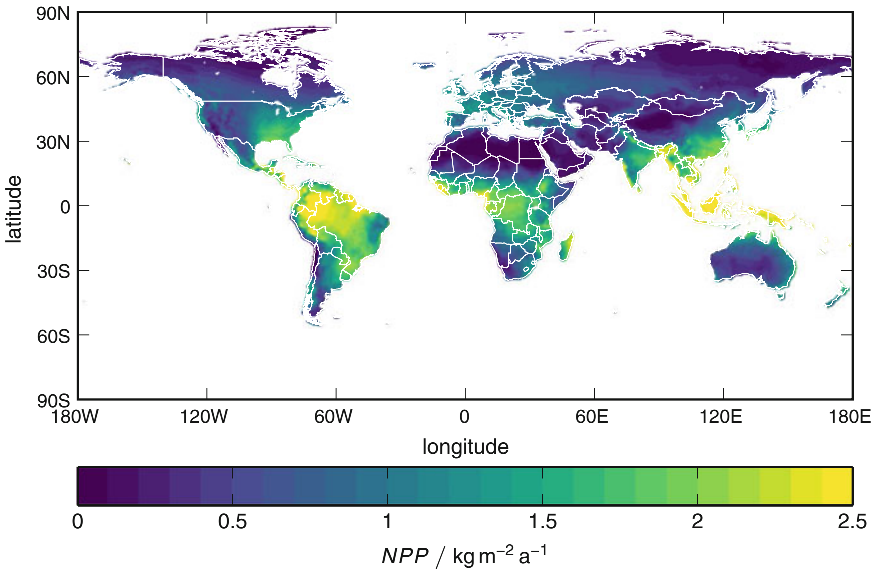


Fig. 3.14 Global distribution of annual net primary production (*NPP*) on land surface for the period 1951–2000, data from http://www.fao.org/nr/climpag/globgrids/npp_en.asp, based on datasets from the Global Precipitation Climatology Centre (GPCC), 0.5° spatial resolution (latitude/longitude)

$$NPP = 3.0\,(1 - \mathrm{e}^{-0.000664\,P}) \tag{3.14}$$

$$NPP = \frac{3}{1 + \mathrm{e}^{1.315 - 0.119\,T_{\mathrm{av}}}} \tag{3.15}$$

NPP is given as dry matter production in kg $\mathrm{m}^{-2}\mathrm{a}^{-1}$ with the annual temperature average T_{av} in °C and the annual precipitation P in mm a^{-1}.

The FAO Environment and Natural Resources Service of the United Nations has developed global climate maps based on the Lieth model. Figure 3.14 shows the *NPP* for the period 1951–2000 based on datasets from the Global Precipitation Climatology Centre (GPCC).

Rate of Photosynthesis Reaction and External Factors

As a photo-biological (or -biochemical) process, photosynthesis is primarily dependent on the availability of solar radiation. As a result, plant growth is an extremely unsteady process, following the cyclic changes of day/night and the seasons. In addition, the actual rate of photosynthesis may be affected by a number of other external factors such as temperature, availability of CO_2, water, and mineral nutrients. Rate expressions are generally based on a first order assumption (in biomass) and on the Monod model, assuming a maximal rate whenever a limiting component is available in sufficient quantity, and simple expressions for the decreasing effects of the limiting components *i* (Eqs. (3.16) and (3.17)).

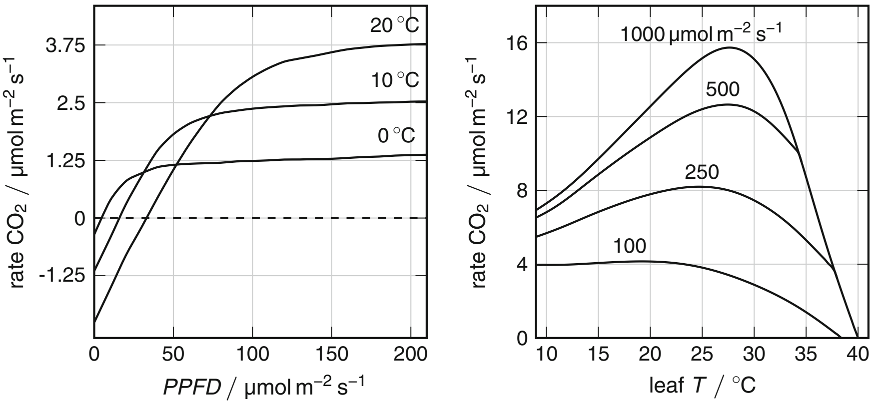


Fig. 3.15 Effects of photosynthetic photon flux density *PPFD* and temperature on photosynthesis rate, *left* example with low *PPFD* (Walter and Breckle 1991; after Schultz 2000, p. 88), *right* example with high *PPFD* (Larcher 2003, p. 137; after Hall 1979)

$$r = \frac{\mathrm{d}c_x}{\mathrm{d}t} = \mu\, c_x \tag{3.16}$$

$$\mu = \mu_{\max}\, \frac{PPFD}{K_{PPFD} + PPFD}\, \frac{c_i}{K_i + c_i} \tag{3.17}$$

With r as the rate expressed in biomass weight increase (or CO_2 consumption, O_2 formation), c_x as the actual amount of biomass (as mass, concentration or other), μ as the specific growth rate, $\mu_{\max}$ as the maximum specific growth rate without limitation, *PPFD* as the photosynthetic photon flux density, c_i as the concentration of limiting component i (CO_2, H_2O, nutrients), and K as the characteristic constant.

The effect of temperature leads to a rate initially increasing and then – after going through a maximum – decreasing with temperature. This can be approximated with a Gaussian function, the shape of which is dependent on the available *PPFD*. The combined effects of temperature and *PPFD* are illustrated with two examples in Fig. 3.15 (conversion *PPFD* to radiative energy flux density $\mathrm{W\,m^{-2}}$ for total solar radiation: factor 0.48 approx.).

In the wavelength spectrum of the incoming solar radiation (see Sect. 3.1) only the range 400–700 nm can be absorbed and used for photosynthesis by green plants (*photosynthetic photon flux density PPFD*). With respect to energy, this represents about 50 % of the solar spectrum. The light response term (*PPFD*) in Eq. (3.17) is a simplification in two ways: (i) At very low or zero values of *PPFD* respiratory release of CO_2 by oxidation of biomass (*respiration*) exceeds the photosynthetic uptake (*assimilation*). Respiration is dominating during dark phases where no or little radiative energy supply by solar light is available (Fig. 3.15 left). (ii) In cases where the photosynthetic apparatus is highly sensitive to light, the light-response curve shows an irradiance optimum and decreasing rates with higher values of irradiance (inhibition at high values of *PPFD*). This is the case, for example, in aquatic plants.

Also indicated in Fig. 3.15 (right) is the characteristic temperature effect on the rate of photosynthesis for an example case: a given plant exhibits, with high solar irradiance, a stronger effect of temperature and higher optimum temperature values than with lower irradiance conditions. In the latter case, *PPFD* is the major limiting factor, and the temperature limitation is less significant. At too low or too high temperatures, the photosynthetic yield declines drastically to the point where plants cease to assimilate CO_2. These cold and heat limitation values vary with the kind of plant. For example, in tropical plants, cold limitation occurs just above freezing, whereas typical plants of the temperate zone can take up CO_2 even at temperatures below 0 °C in the atmosphere.

The supply of CO_2 may become limiting – for the actual CO_2 concentration level in the atmosphere – if irradiance levels are high, e.g. around noon in locations at lower latitude. Among the mineral nutrients required for plant growth are nitrogen, phosphorus, particular ions (such as K^+, Ca^{2+}, Mg^{2+}, Cl^-) and trace elements (such as iron, copper, zinc). In soils not seriously deficient in particular nutrients, the availability of minerals generally is less critical for photosynthesis than climatic factors.

3.5 Energy Balance and Climate

Incoming energy from the Sun, absorption of radiation by the atmosphere, and the reflective properties of the Earth's surface determine the climatic conditions on Earth. The biosphere plays a decisive role as it co-determines (i) the albedo through the vegetation on the land surface and cloud formation, (ii) the energy transport from surface to atmosphere by evapotranspiration and (iii) the consumption and formation of greenhouse gases such as carbon dioxide. The mathematical description of the global climatic conditions on Earth including the spatio-temporal distribution, the explanation of the historic developments as well as predictions for the future is a tremendous challenge that requires profound understanding of the relevant physical, chemical, and biological principles as well as sophisticated numerical techniques and the most efficient computers. It is beyond the scope of this book to give a full overview about the state of the art in climate modeling and the required future developments.

In this chapter, we have selected a few simple feedback models in order to describe important general aspects of the global climate system. One feedback mechanism for consideration is caused by the fact that the concentration of water vapor increases with rising temperature. Since water vapor contributes strongly to the greenhouse effect (cf. Table 3.1) causing a further temperature increase, a powerful positive feedback mechanism is established. On the other hand, higher temperatures may lead to enhanced cloud formation giving rise to stronger reflection of incoming solar radiation. The selected models cover the possible development of multiple steady states of the climate system thus predicting extreme conditions on Earth. On the other hand, it can be shown that other equally important feedback mechanisms may lead to self-stabilizing behavior of the Earth system. Finally, the structure of the global climate models that are presently under development is briefly summarized.

3.5.1 Snowball Earth: Ice-Albedo Feedback and Multiple Climate States

It was discussed earlier that the albedo of the Earth's surface exhibits a strong geographical variation (see Fig. 3.10). While the albedo of ocean surfaces is only around 10 %, it may reach more than 60 % on surfaces covered with ice. Neglecting any spatial distribution of the albedo, it is interesting to discuss the influence of the average albedo value on the resulting mean surface temperature of a planet. Figure 3.16 schematically shows the relationship between average planetary albedo and resulting temperature. If the planet would be completely ice-free, a low albedo and consequently a high emitted radiative flux density and temperature result. For the case of Earth completely covered with water ($a = 0.1$), the effective temperature, neglecting the greenhouse effect, amounts to $T_{\text{eff}} = 271\,\text{K}$ (cf. Box 3.1). In contrast, a completely ice-covered Earth ($a = 0.6$) has a temperature of only 221 K. Both states are stable solutions of a simple overall energy balance for the Earth and Fig. 3.16 also reveals that a third solution with partial coverage of ice could exist. These multiple states are typical for complex systems including linear and nonlinear dependencies

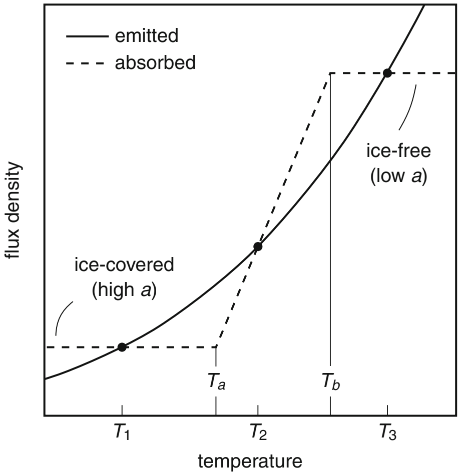


Fig. 3.16 Three equilibrium temperature solutions for ice-free (low albedo), completely ice-covered (high albedo), and partially ice-covered Earth for intermediate temperatures between T_a and T_b, after McGuffie and Henderson-Sellers (2005)

of properties and were discussed earlier for the example of a cooled chemical reactor in which an exothermic reaction proceeds (see Fig. 1.14).

Earth has often exhibited an intermediate state with ice caps covering the most northern and southern parts of the planet. If one now assumes that the climate is in the beginning of an ice age, e.g. caused by decreasing solar activity or falling greenhouse gas concentrations, the ice would expand into regions that were previously covered by water or vegetation. Consequently, the albedo in these regions strongly increases and reduces the fraction of the solar radiation absorbed by the surface. This leads to further cooling and subsequent enlargement of the ice covered area. It is evident that this positive feedback may lead to an ice age with probably a completely ice-covered *snowball* Earth.

This *ice-albedo feedback* was first discovered by Budyko (1969) and Sellers (1969). Both used very simple steady-state models including the absorbed solar energy, the emitted energy from the surface, and the horizontal energy transport by atmosphere and ocean. These three terms are functions of both latitude x and surface temperature T_s. The energy balance (Eq. (3.18)) can be written as:

$$J_{\text{abs}}\,(x, T_s) = J_{\text{em}}\,(x, T_s) + J_{\text{horiz}}\,(x, T_s). \tag{3.18}$$

The absorbed flux density is proportional to the incoming solar radiation and the local albedo, for which an abrupt transition from a low value (e.g. 0.3) for ice-free to a high value (e.g. 0.6) for ice-covered surface was assumed. The emitted flux density is influenced by the enhanced blackbody radiation according to the Stefan–Boltzmann law, but also through changes of the greenhouse effect induced by the temperature-dependent concentration of water vapor. The horizontal transport term can be described in different ways such as by assumption of a linear dependence on the difference between the local and the global average temperature. McGuffie and Henderson-Sellers (2005) formulated a simple version of the models developed earlier by Budyko (1969) and Sellers (1969). Equation (3.18) then results in the following relationship:

$$J_s(x)\,(1 - a(x)) = (A + B\,T_s(x)) + k_{\text{horiz}}\,(T_s(x) - \overline{T_s}). \tag{3.19}$$

Here, $J_s(x)$ is the average annual solar flux density or insolation (related to the flat shadow area πr^2 of the Earth) at latitude x, k_{horiz} a transport coefficient, $\overline{T_s}$ the average global surface temperature, and A and B constants describing the longwave radiation loss of the surface. For the albedo, a simple step function with values of 0.3 for ice-free and 0.6 for ice-covered surface (at temperatures of $T_s(x)$ less than $-10\,°\text{C}$) is assumed. Figure 3.17 shows some examples of calculated global temperature and albedo distributions. Assuming the present day insolation ($1370\,\text{W}\,\text{m}^{-2}$, relative value 1.0 in Fig. 3.17) results in ice caps extending to the 70 to 80 latitude zones with temperatures of about $-13\,°\text{C}$, a temperature of 24 °C close to the equator, and an average global temperature of 15 °C. A relatively small increase of the insolation to a relative value of 1.05 already leads to complete melting of the ice caps and an increase of local and average global temperatures by about 5 K. To achieve a completely ice-covered Earth, the insolation must be reduced to 0.7, in that case the calculated average global temperature is only $-18\,°\text{C}$.

These simple energy-balance models explain why multiple solutions of the Earth's energy balance exist and also provide a qualitatively correct distribution of ice coverage and temperatures versus latitude (cf. Fig. 3.12 and Table 3.2). However, it is difficult to see how Earth could have recovered from a possible total glaciation. Indications of such extreme global climate conditions were actually found in sediments during the 1980s (Sumner 1987). In an attempt to improve the original ice-albedo feedback models in order to explain the obvious fact that the complete glaciation

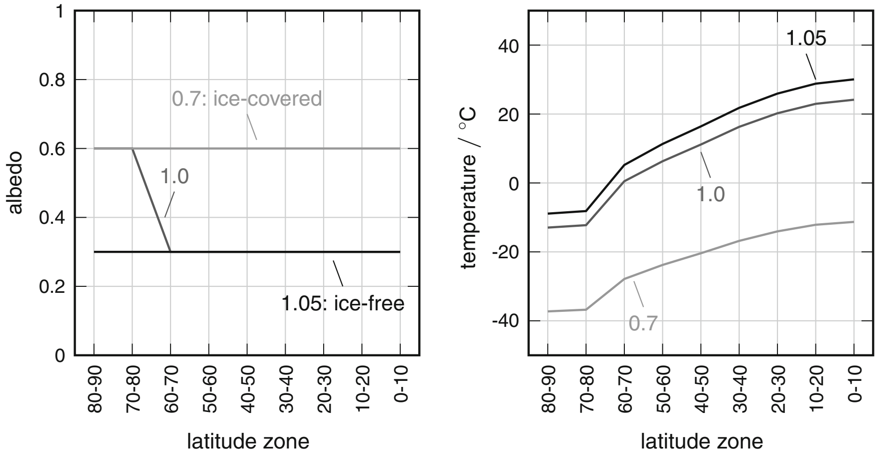


Fig. 3.17 Albedo (*left*) and temperature (*right*) versus latitude for three different assumed insolation values ($k_{\text{horiz}} = 3.86\,\text{W}\,\text{m}^{-2}\text{K}^{-1}$, $A = 204\,\text{W}\,\text{m}^{-2}$, $B = 2.17\,\text{W}\,\text{m}^{-2}\text{K}^{-1}$)

of the Earth is reversible, Caldeira and Kasting (1992) included the carbon dioxide emissions from volcanoes. With this elegant extension of the model it was possible to describe reversible cycles of glaciation and deglaciation (Fig. 3.18).

In the case of an instability of the partially ice-covered solution (points 1 and 7 in Fig. 3.18), e.g. by increased carbonate weathering during the time with more continents placed in the tropics and a resulting decreased CO_2 concentration, the Earth system is driven to the completely ice-covered state (point 3) and would remain there without any additional feedback mechanisms. However, volcanic outgassing in combination with a decreased carbon dioxide uptake by the ocean and through weathering at the then very low Earth temperatures, strongly increases the atmospheric CO_2 concentration and deglaciation (at point 4) is finally initiated. Then, high carbon dioxide concentrations and a low global albedo lead to an extreme greenhouse effect for some time (point 5). Finally, enhanced weathering causes lowering of the CO_2 concentration until polar ice caps reform and ice lines return to the starting point.

3.5.2 Simple Models for the Self-Regulating Behavior of the Earth System

Watson and Lovelock (1983) have proposed a simple model to explain how the biosphere might be able to maintain the Earth in a stable climatic state. The authors did not try to explain the full complexity of the Earth system, but rather constructed an artificial world that exhibits self-regulating properties believed to be important for the Earth. *Daisyworld* is a planet without the greenhouse effect or clouds on which two plants with different reflective properties exist. One species is darker (*black*) than

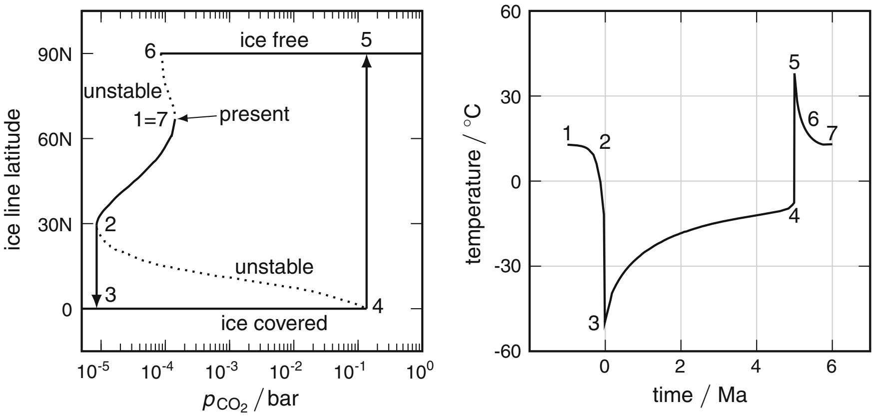


Fig. 3.18 Ice-concentrationas a function of the atmospheric carbon dioxide oncentration (*left*) and resulting global average temperatures (*right*) according to simple energy-balance calculations, after Hoffmann and Schrag (2002), numbers indicate relationship between position of ice-line latitude and temperature

the ground it grows on and reflects less sunlight while the other species is lighter (*white*) and reflects light more strongly. The daisy populations are governed by the following differential equations (Eq. (3.20)).

$$\begin{aligned}\frac{\mathrm{d}A_\mathrm{W}}{\mathrm{d}t} &= A_\mathrm{W}\,(bA_\mathrm{F} - d)\\ \frac{\mathrm{d}A_\mathrm{B}}{\mathrm{d}t} &= A_\mathrm{B}\,(bA_\mathrm{F} - d)\end{aligned} \tag{3.20}$$

Here, A_B and A_W are the fractional areas covered by black and white daisies, b the growth rate, and $d = 0.3$ the death rate of the daisies. The fractional area of uncovered fertile ground A_F is obtained from Eq. (3.21).

$$A_\mathrm{F} = 1 - A_\mathrm{W} - A_\mathrm{B} \tag{3.21}$$

The growth rate Eq. (3.22) of both types of daisies is assumed to be a parabolic function of the local temperature T_i of either black or white daisies. It reaches its maximum at 22.5 °C and becomes zero at 5 and 40 °C, respectively.

$$b = 1.0 - 0.0003265\,(295.5\,\mathrm{K} - T_i)^2 \tag{3.22}$$

The global energy balance (Eq. (3.23)) for the planet yields

$$\sigma\,T_\mathrm{av}^4 = (1 - a_\mathrm{av})\,J_\mathrm{solar} \tag{3.23}$$

with T_av the average global temperature and a_av the area-weighted average (Eq. (3.24)) of the albedos of white daisies, black daisies, and bare ground.

$$a_\mathrm{av} = A_\mathrm{W}\,a_\mathrm{W} + A_\mathrm{B}\,a_\mathrm{B} + A_\mathrm{F}\,a_\mathrm{F} \tag{3.24}$$

In order to reach familiar temperature values during the calculations, a higher solar radiation of $J_\mathrm{solar} = 917\,\mathrm{W\,m^{-2}}$ than the present value on Earth was selected to compensate the missing greenhouse effect of the model planet. The balance for the local temperatures T_i (Eq. (3.25)) in regions with different surface covering A_i and albedo a_i takes into account the horizontal heat transfer between the two regions.

$$T_i^4 = q\,(a_\mathrm{av} - a_i) + T_\mathrm{av}^4 \tag{3.25}$$

The heat transfer parameter q is in the range between 0 (perfectly efficient heat transfer that results in $T_i = T_\mathrm{av}$) and $q = \frac{J_\mathrm{solar}}{\sigma}$ (perfect isolation between black and white daisies).

Figure 3.19 shows selected steady-state solutions for the Daisyworld model. The growth of a population of daisies with an albedo equal to the bare ground ($a = 0.5$) and the planetary temperature as functions of the normalized solar irradiation (*luminosity*) are depicted in diagrams (a) and (c) on the left hand side of the figure. As expected, the population reaches its maximum at the optimum temperature of 22.5 °C and becomes extinct in the cases of too low or too high temperatures. The planet with black and white daisies, however, shows a remarkably stable temperature over the entire region of solar irradiations in which daisies can exist (Fig. 3.19b, d). This is caused by the fact that luminosity changes affect the proportion of black or white daisies in the total population. At low solar luminosity, black daisies are favored because they are warmer than the emission temperature of the planet without life. As the luminosity increases, white daisies grow at the expense of the black species and the resulting increase of the average planetary albedo reduces the temperature response.

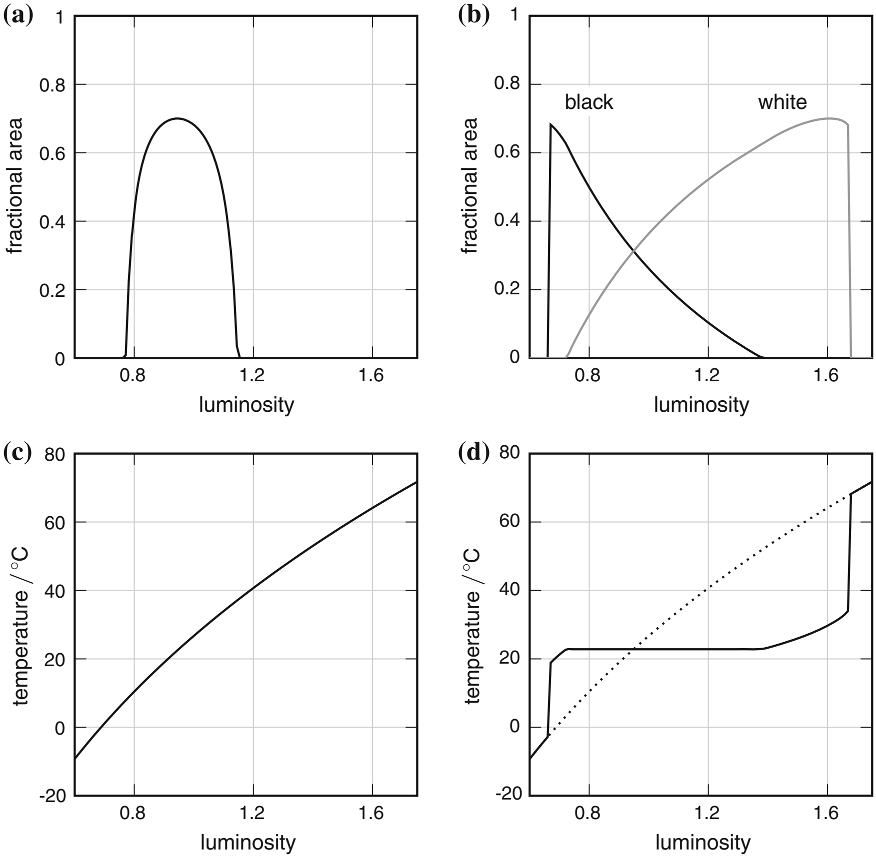


Fig. 3.19 Calculated steady-state areas of world with neutral daisies ($a = 0.5$) and for a population of black ($a_\mathrm{B} = 0.25$) and *white* ($a_\mathrm{W} = 0.75$) daisies as a function of solar luminosity (*top*) and corresponding planetary temperatures (*bottom*), *dotted line* shows temperature for planet without life ($a = 0.5$) for comparison, values calculated with $q = 0.2\,\frac{J_\mathrm{solar}}{\sigma}$ (Watson and Lovelock 1983), luminosity: normalized solar irradiation, for further details see text

Although Daisyworld is not a realistic model for the Earth and has been sometimes criticized for its simplicity, it clearly illustrates how the biosphere might influence the conditions on Earth and the stability of the climate. Hartmann (1994) has pointed out that the biosphere acted like white daisies during phases where it reduced the CO_2 content of the atmosphere and thus cooled the Earth (Sect. 1.2.2). Kleidon (2009) has discussed thermodynamic models to predict the stabilizing behavior of the Earth system. Figure 3.20 (top) shows how beneficial planetary conditions could result from the contrasting effects of surface temperature on ice albedo and cloud albedo. In a similar way, the effects of land vegetation on surface albedo and evapotranspiration could result in a state with optimal overall absorption of solar radiation (Fig. 3.20, bottom).

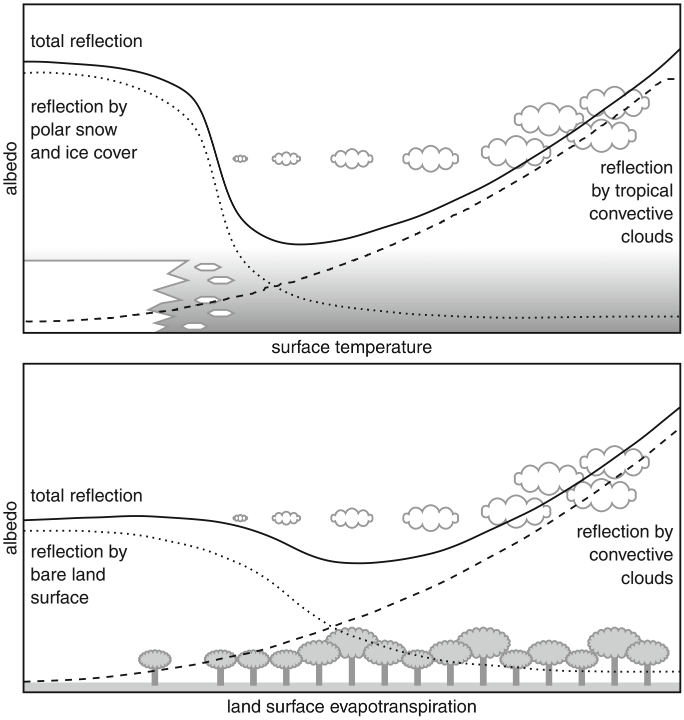


Fig. 3.20 Maximum absorption of solar radiation at planetary scale (*top*) as a result of the contrasting effects of surface temperature on ice and cloud albedos and at the land surface (*bottom*) resulting from the contrasting effects of vegetation on land albedo and evapotranspiration on absorption of solar radiation (inspired by Kleidon 2009, Fig. 6)

3.5.3 Global Climate Models

In contrast to the simple feedback Earth models presented in the previous Section, global climate models (GCM) allow for a realistic assessment of all relevant phenomena on Earth including the real flow patterns in the atmosphere and the ocean. Hartmann (1994) has pointed out that the source *global climate model* of the acronym should be preferred over the often used term *general circulation model*, as circulation is only one of many key components in modern climate models. Selected components of a GCM are schematically depicted in Fig. 3.21.

Global climate models are based on the general principles of fluid dynamics and thermodynamics and include all the processes in the climate system such as radiation, energy transfer by winds and ocean currents, cloud formation as well as evaporation and precipitation of water. The calculations are carried out for individual gridboxes on the order of 100 km in the horizontal and 1 km – with more densely spacing near the lower boundary – in the vertical dimensions (Fig. 3.22). The model equations are

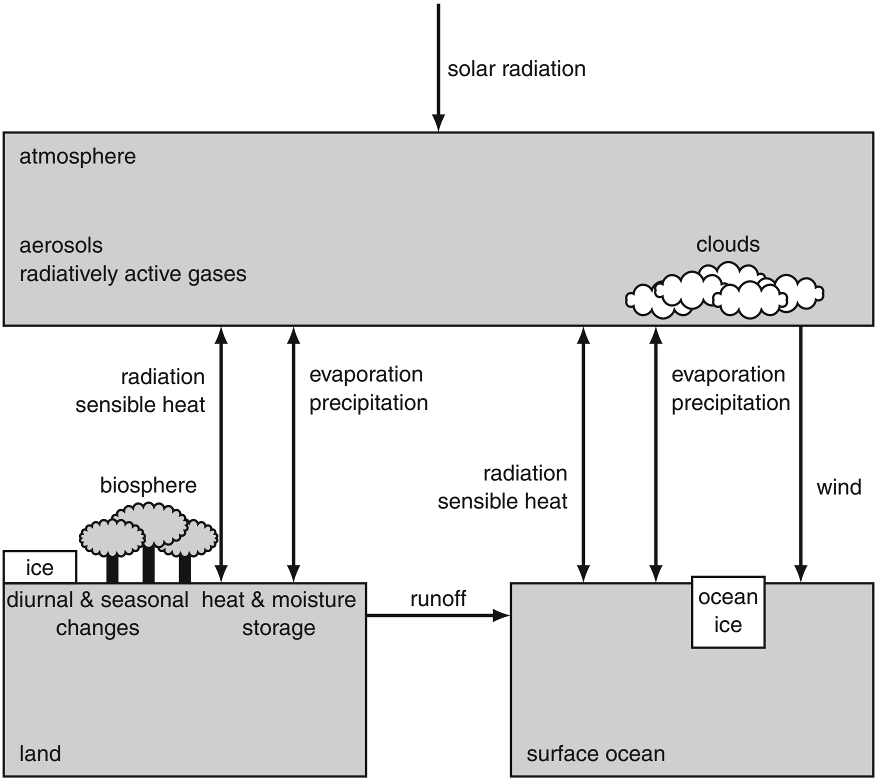


Fig. 3.21 Structure of a global climate model coupling atmosphere, land and ocean with selected important processes

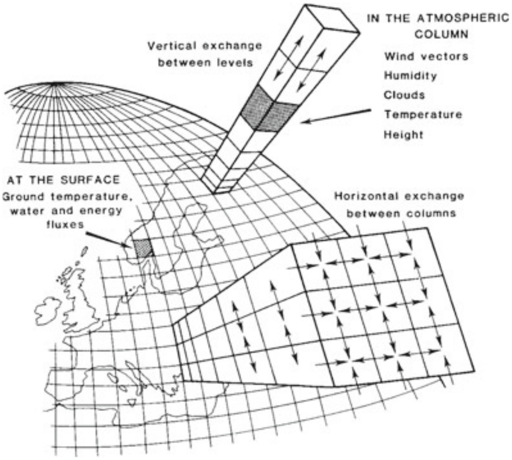


Fig. 3.22 Conceptual structure of a dynamic, three-dimensional global climate model for the Earth's atmosphere, from Schlesinger (1997), after Henderson-Sellers and McGuffie (1987), published with kind permission of © Academic Press, 1997, all rights reserved

solved for atmosphere, land surface, and ocean in each gridbox over the entire globe as a function of time.

Cloud properties and their associated convective motions are relevant on a spatial scale that is much smaller than the gridsize of climate models. These and other sub-grid-scale phenomena must be determined from the properties of the respective gridbox by using adjustable parameters.

Modern GCMs allow for a coupling of ocean and atmosphere including terrestrial processes and sea ice dynamics. They are continuously improved by including further elements such as chemical or biological processes and also by the increasing computational speed which allows for a better spatial resolution during simulations. These models have been proven to be capable of simulating ancient climates with relatively good accuracy and are – despite their still existing limitations – generally believed to provide quantitative estimates of future climate change, especially on larger scales (IPCC 2007b).

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Chapter 4
Global Material Cycles

This chapter discusses prominent examples of global material cycles. This is of major significance in order to understand potential perturbation of the natural material cycles caused by man's production or use of energy. As selected examples, carbon, water, nitrogen and oxygen cycles will be treated, and in addition aspects of some other material cycles (sulfur, phosphorus, chlorine) as well as interactions of cycles. Significant simplifications must be used in order to focus on the major points.

The Earth as a closed system (according to Sect. 1.2) is represented in the present discussion by a selection of several open (sub-)systems which exchange material species (and energy) by various processes (chemical reactions, transport processes, etc.). In the subsequent figures, subsystems are always displayed as boxes. Components in these subsystems may include chemical species and/or different physical phases (vapor, liquid, solid). Flows of species (potentially connected to energy flows) are depicted as arrows and may be linked to (bio)chemical reactions, phase changes or transport processes across subsystem boundaries. According to the rates of flow and to the reservoir inventories of individual components, a formal residence time τ_{ij} can be defined as a characteristic quantity to represent a characteristic time scale for component i in a reservoir j (Eq. 4.1).

$$\tau_{ij} = \frac{m_i}{F_{m,ij}} \tag{4.1}$$

All examples discussed in the following will be simplified as a (quasi-)steady-state situation, with time-averages of all annual flows involved. Rates of individual flows will differ significantly, based on different characteristics of the individual processes (e.g. chemical reaction, mass transfer, phase change, etc.). Connections between material flows and energy flows have to be taken into account for processes where significant energy changes/heat effects are involved (chemical reactions, phase transitions).

G. Schaub and T. Turek, *Energy Flows, Material Cycles and Global Development*, Environmental Science and Engineering,
DOI 10.1007/978-3-319-29495-7_4

4.1 The Carbon Cycle

The carbon cycle determines, in a significant manner, the global climate via atmospheric concentrations of the greenhouse gases CO_2 and CH_4 (Chap. 3). It is therefore of central interest to the processes in the biogeosphere (Schlesinger 1997). Living organisms are composed primarily of carbon, so estimates of the global production and destruction of organic carbon give an overall index of the health of the biosphere. Photosynthesis accounts for the presence of molecular O_2 in the atmosphere, thus closely linking the carbon and oxygen cycles on Earth, with the presence of O_2 setting the redox potential for organic metabolism in most habitats. The aim of this section is to discuss how humans have altered the global cycle of carbon, causing the atmospheric concentration of CO_2 to rise to levels that have not been experienced during the recent evolutionary history on Earth.

The carbon species considered in the subsequent discussion will be either gaseous (CO_2, CH_4), solid (carbonates, the total of organic carbon in various species in living biomass, soil), or liquid (CO_2 dissolved as CO_3^{2-}/HCO_3^- in H_2O). A model of the current global carbon cycle is shown in Fig. 4.1, with average values for significant reservoir inventories and annual flows for the time period 2000–2009 (IPCC 2013b). This is a dynamic system driven by the radiative energy input from the Sun.

Reservoirs

Among the reservoirs shown in Fig. 4.1, the atmosphere exhibits a small carbon inventory (829 Gt, average value during 2000–2009, equivalent to a volume concentration of about 390 ppm) compared to organic carbon in terrestrial and marine biomass (1953–3053 Gt). Ocean reservoirs are divided into surface ocean and intermediate/deep waters (900 and 37 100 Gt). The largest reservoir represents the sediments (20×10^6 Gt), containing a large amount of inorganic carbonates and organic carbon-containing minerals, with an average organic carbon content of 0.5 wt%. Among the latter, the fraction with a high concentration in organics represents the fossil organic raw materials used today for energy and chemistry applications (petroleum, natural gas, coal, with around 70 % coal). Interestingly, more CH_4 is stored in underground sediment space as natural gas than is found as a minor constituent in the atmosphere (see Sect. 2.2.2). The fossil organic raw materials have been formed over long periods of the Earth history (most recent 200 million years), and they contain – besides *conventional* (high) qualities – *unconventional* lower-quality materials, richer in inorganic material (e.g. tar sand, high-ash coals etc.). The origin of these fossil organic raw materials are large amounts of biomass buried underground that have seen favorable time-temperature-pressure histories in the absence of atmospheric oxygen. In this way, slow biochemical and chemical conversion reactions releasing CO_2, H_2O, and CH_4 could occur in a process that for coal is called coalification (van Krevelen 1961). The resulting material can be seen as stored chemical energy. It has

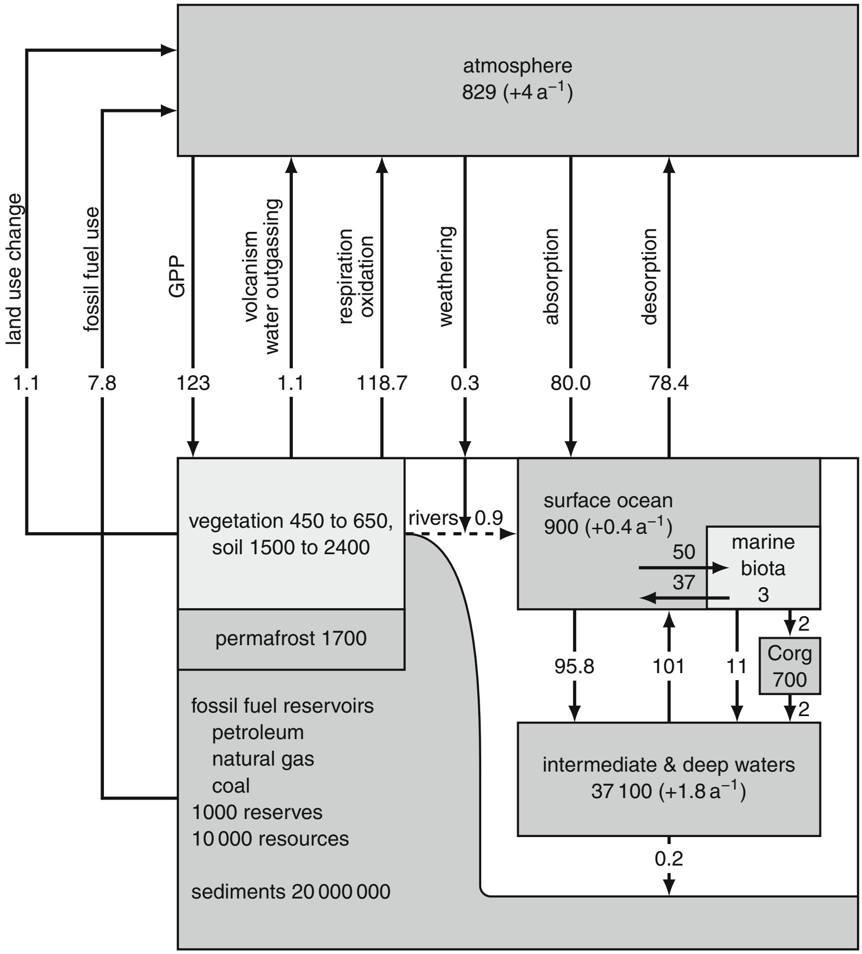


Fig. 4.1 Global carbon reservoirs and flows, estimated values in Gt or Gt a^{-1} as average values during period 2000–2009, *sources* Schlesinger (1997), IPCC (2013b), Siegenthaler and Sarmiento (1993), Bolin (1970), reserves/resources: rounded values, see Sect. 6.1.1 and Fig. 7.14

a higher energy density than the original biomass, due to the loss in oxygen content. The total amount of carbon in the biogeosphere is dominated by the reservoir of the sediments (20×10^6 Gt).

Processes (Natural and Caused by Humans)

Among the most significant processes that continuously remove CO_2 from the atmosphere are photosynthesis (gross photosynthesis productivity GPP 123 Gt a^{-1}) and absorption in surface ocean waters (80 Gt a^{-1}). These flows have counterparts in the reverse direction in the form of living organism respiration and oxidation of soil and detritus (118.7 Gt a^{-1}) and desorption from the ocean surface (78.4 Gt a^{-1}). The global flow of carbon in GPP can be compared to the real growth of biomass, equivalent to net productivity of photosynthesis *NPP* (172.5 Gt a^{-1} dry biomass (Table 3.3)), with about 50 % carbon content (Table 5.10), leading to a net carbon flow in *NPP* of 86.3 Gt a^{-1}.

Carbon flows caused by humans include the use of fossil fuels and land use changes (7.8 and 1.1 Gt a^{-1} respectively). In addition, there are weathering processes and sink processes (residual terrestrial sink) resulting as uncertainty from carbon mass balance treatment. In the ocean waters, carbon-involving processes include photosynthesis, carbonate-forming chemical reactions and transport processes caused by convection, diffusion, and sedimentation.

The processes involving carbon each exhibit characteristic rates (e.g. as Gt a^{-1} or kg a^{-1} m^{-2}). These rates are determined by the underlying physical or chemical mechanisms and are significant for the resulting (quasi-)steady-state distribution of carbon among the reservoirs. Characteristic rates can also be expressed by time scales, i.e. characteristic times, indicating the time required for achieving a degree of conversion or disappearance of a gradient.

The formal residence time (as defined in Eq. (4.1)) of carbon species in the atmosphere is about 4 a, whereas in the *geochemical cycle* of sediment formation the formal residence time is 100×10^6 a (or 3×10^6 a including fossil fuel use).

Current Changes and Pre-industrial Carbon Cycle

Processes caused by humans that affect the global carbon cycle include changes in land use (agriculture, forestry, destruction of forest), and the large scale production and use of fossil fuels (use via combustion, after raw material processing, chemical upgrading).

Carbon inventory in the atmosphere has increased to more than 220 Gt above its pre-industrial level, as can be seen from Figs. 4.1 and 4.2. This increase is equivalent to about 50 % of the cumulative anthropogenic CO_2 emissions from fossil sources ((375 ± 30) Gt C between 1750 and 2011) and from change in land use ((180 ± 80) Gt C, (IPCC 2013b)). Accordingly, carbon dioxide concentration has increased from 280 to 390 ppm in 2005. The annual mean CO_2 growth rate was significantly higher for the most recent period from 2002 to 2011 (4.3 Gt a^{-1}) compared to the value during the 1990s (3.1 Gt a^{-1}, Table 4.2).

Annual emissions of CO_2 from fossil fuel burning and cement production increased from 0 prior to the year 1750 to 6.4 Gt a^{-1} (as carbon) in the 1990s to 7.8 Gt a^{-1} for 2000–2009 and reached a value of 9.5 Gt a^{-1} in 2011 (IPCC 2013a). Determination of the flow value of CO_2 to the atmosphere due to land use change ((1.1 ± 8) Gt a^{-1} for 2000–2009, (IPCC 2013b)) is based on a combination of techniques. However, there is continuing uncertainty in the net CO_2 emissions due to land use change. A rough orientation of phytomass (B) inventories of different biomes is

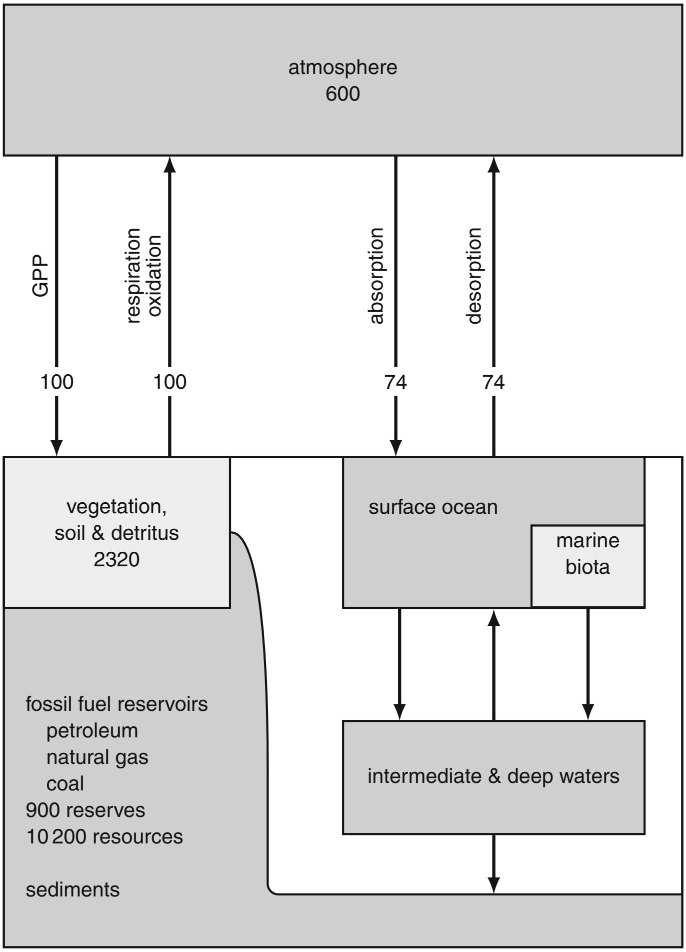


Fig. 4.2 Global carbon reservoirs and flows, estimated values in Gt or Gt a^{-1} as average values before industrialization (1750), only values significantly different from Fig. 4.1, *sources* IPCC (2007), Siegenthaler and Sarmiento (1993)

given in Table 4.1. These values allow the estimation of carbon release effects into the atmosphere due to land use changes.

As an example of recent research activities, plant diversity in land vegetation is seen as an important aspect of carbon inventories affected by land use change (Lange et al. 2015). As the mechanisms underlying the plant diversity effects on soil carbon storage are poorly understood, a long-term grassland biodiversity experiment presently addresses this relationship (The Jena Experiment). The data collected in systematic variations of grassland vegetation indicate that higher plant diversity increases carbon inputs into the microbial community resulting in both increased microbial activity and carbon storage. Increases in soil carbon were related to the

Table 4.1 Phytomass inventories (B, dry mass) and annual net primary production (*NPP*, dry biomass) of different biomes (after Larcher 2003, pp. 166–167, based on various sources)

	B kg m^{-2}	*NPP* $\text{kg m}^{-2}\,\text{a}^{-1}$	Fraction of Earth surface %
Oceans	<0.01	<0.4	65.1
Continental shelf	0.01–0.1	0.2–0.6	5.2
Tidal zone, mangroves, marsh and swamp	10–50	1–6	0.5
Rain forest, warm regions	40–80	1–3.5	3.3
Temperate forest	10–50	0.5–2.5	2.4
Rock, ice	<0.3	<0.001	4.7
Shrubland, drought-deciduous forest, savanna	2–15	0.2–2.5	6.0
Grassland, steppe	2–5	0.2–2	1.8
Open vegetation, tundra, desert	0–2	<0.04	7.4

Table 4.2 Global net change of atmospheric carbon inventory per year and related annual carbon flows in Gt a^{-1} carbon (IPCC 2013b)

	1980–1989	1990–1999	2000–2009	2002–2011
Emissions (fossil + cement)	5.5 ± 0.4	6.4 ± 0.5	7.8 ± 0.6	8.3 ± 0.7
Atmospheric increase	3.4 ± 0.2	3.1 ± 0.2	4.0 ± 0.2	4.3 ± 0.2
Net ocean-to-atmosphere flux	-2.0 ± 0.7	-2.2 ± 0.7	-2.3 ± 0.7	-2.4 ± 0.7
Net land-to-atmosphere flux	-0.1 ± 0.8	-1.1 ± 0.9	-1.5 ± 0.9	-1.6 ± 1.0
Land use change flux	1.4 ± 0.8	1.5 ± 0.8	1.1 ± 0.8	0.9 ± 0.8
Residual terrestrial sink	-1.5 ± 1.1	-2.6 ± 1.2	-2.6 ± 1.2	-2.5 ± 1.3

enhanced accumulation of recently fixed carbon in high-diversity plots. Accordingly, a loss in plant diversity due to change in land use leads to a shift of carbon stored in the soil into the atmosphere.

The removal of CO_2 from the atmosphere involves different processes with different time scales. About 50 % of the CO_2 increase will be removed from the atmosphere within 30 years, and an additional 30 % will be removed within a few centuries. The remaining 20 % may stay in the atmosphere for many thousands of years (IPCC 2007). Inter-annual and inter-decadal variations in the growth rate of atmospheric CO_2 are dominated by the response of the land biosphere to climate variations. Evidence of decadal changes is observed in the net land carbon sink, with estimates of $(1.5 \pm 1.1)\ \text{Gt a}^{-1}$, $(2.6 \pm 1.2)\ \text{Gt a}^{-1}$, and $(2.6 \pm 1.2)\ \text{Gt a}^{-1}$ for the 1980s, 1990s and 2000–2009 time periods, respectively (IPCC 2013b).

Average values of the ocean CO_2 uptake during the 1990s are in the range 1.5–2.9 Gt a^{-1} (Table 4.2). The cumulative CO_2 uptake has lowered the average ocean pH value (equivalent to an increased acidity) during this period by approximately 0.1 since 1750. This may have consequences for marine ecosystems with shell-forming organisms and carbonate sediments.

Conclusion

The global carbon system shows that fossil CO_2 emissions due to human activities are released to the relatively small reservoir of the atmosphere. During the past decades, about 50 % of the fossil CO_2 emissions remained in the atmosphere, leading to an increase of the CO_2 concentration by about 0.5 % per year. For the other 50 %, there are sink terms in the ocean and in the terrestrial organic carbon reservoir. It is evident that given the mechanisms described, the release of large portions of the fossil organic raw materials (petroleum, natural gas, coal) will lead to significant increases in the carbon inventory of the atmosphere. As an extreme, total amounts of fossil organic carbon in petroleum, natural gas, coal exceed the present atmospheric carbon inventory by a factor of more than 2 (see Fig. 7.14). Given the connection between CO_2 (and CH_4) atmospheric inventories and the global climate (see Sects. 2.2.2 and 2.2.3), there is a strong incentive to decouple energy supply for human societies from fossil organic material combustion.

4.2 The Oxygen Cycle

The presence of large amounts of molecular oxygen in the atmosphere is a unique feature of Earth and one of the most prominent signs of its non-equilibrium state. On a lifeless Earth only small amounts of O_2 could be formed through photolysis of water vapor in the upper atmospheric regions. Oxygen started to accumulate in the atmosphere as the production during oxygenic photosynthesis (React. (3.12)) exceeded O_2 consumption, e.g. by reaction with reduced minerals such as FeS_2, over long periods of time. The present atmospheric oxygen mass of 1.19×10^6 Gt is only a small part of the overall O_2 mass produced by photosynthesis (cf. Fig. 2.4). The largest fraction by far was consumed during the oxidation of pyrite to iron oxides and sulfate (Schlesinger 1997).

As a result of the continuous transformation of carbon dioxide to oxygen containing organic matter, the sediments are now an even larger (organic) oxygen reservoir than the atmosphere (see Fig. 4.3). While atmospheric oxygen concentration strongly increased in earlier geologic times, it remained relatively constant between 5 and 35 vol% during the last 600 Ma (Petsch 2005). This is because the oxygen producing and consuming flows (gross primary production vs. respiration as well as oxidation of organic and inorganic matter) have been more or less in balance. Taking these flows into account, the mean residence time of oxygen in the atmosphere amounts to about 4000 a. In addition to the chemical flows, there is a continuous physical exchange of oxygen between the atmosphere and the ocean through dissolution and outgassing.

The major anthropogenic change to the global oxygen cycle is the burning of fossil fuels that requires a stoichiometric O_2 amount depending on the elemental composition of the fuels used. Although the corresponding flow rate is quite high compared to the oxygen flow caused by inorganic weathering, there is little danger

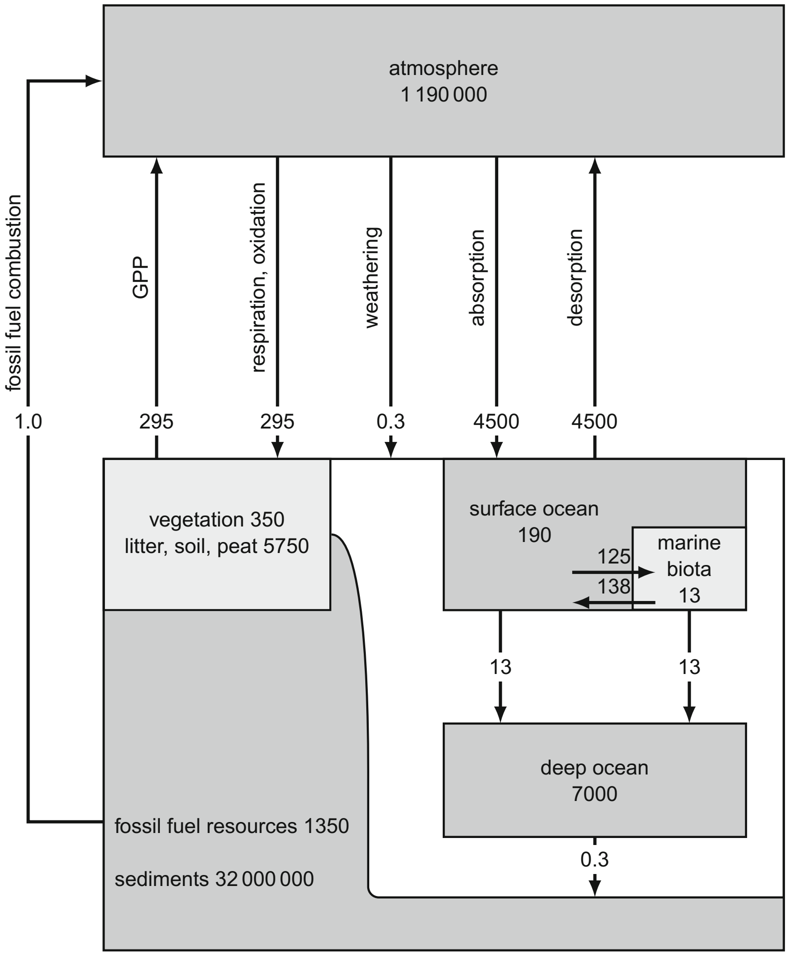


Fig. 4.3 Reservoirs and annual global flows of oxygen in Gt or Gt a^{-1}, data from Keeling et al. (1993), except organic oxygen in fossil fuel resources and flow of oxygen by fossil fuel combustion calculated with 10 000 Gt carbon and molar oxygen-to-carbon ratio of 0.1

of a significant decrease in atmospheric O_2 concentration through human activities even if all fossil fuels would be totally oxidized without any compensation by enhanced photosynthesis. Assuming that fossil fuels containing 10 000 Gt carbon with an average elemental composition of CH_2 were burned, the O_2 concentration would decrease only by about 0.7 vol% without detrimental effect to the biosphere. However, the overall amount of oxygen (present as O_2 and CO_2) in the atmosphere slightly increases, because fossil fuels also have a certain oxygen content.

4.3 The Water Cycle

The chemical species H_2O exists on Earth in the three physical states: vapor, liquid, and solid. This is due to the temperature/pressure conditions at the Earth's surface, characterized by the proximity to the H_2O triple point (273 K, 0.01 bar). In this respect, the Earth has a unique position in the solar system (see Sect. 2.1). The existence of liquid water is a prerequisite for the evolution of all the forms of life typical of the Earth's biogeosphere. Given the polar behavior of H_2O molecules, liquid water can serve as a solvent for ionic or polar species. Thus it can act as a reservoir and transport medium for species participating in metabolic processes, and also as medium with appropriate thermal capacity and transport properties. H_2O also acts as reactant in photosynthesis reactions (see Sect. 3.4). The characteristic polar behavior of H_2O molecules is also the reason for the relatively high values of heat of vaporization/condensation (2450 J g^{-1}) and heat of melting/crystallization (340 J g^{-1}). If the corresponding phase transitions occur in different locations (due to transport of water vapor in the atmosphere) this represents a significant transport of energy in the Earth's climate system.

Global H_2O Cycle – Reservoirs and Processes

By far the largest fraction of the total H_2O available on Earth is in liquid form (97 %, Schlesinger 1997). The ocean contains about 99 % of the liquid water, with the remaining amounts in ground and soil waters (Fig. 4.4). Ocean waters represent an amount of 1.35×10^9 Gt. The amounts of solid H_2O (ice) and gaseous H_2O (vapor in the atmosphere) represent only about 2 % and 10 ppm, respectively, of the total H_2O available on Earth.

The circulation of H_2O due to phase transition and liquid and vapor phase transport is the largest movement of a chemical substance at the surface of the Earth. Huge flows result from evaporation – mainly from the ocean surface – and condensation as rainfall. Within the atmosphere, there is a net flow of H_2O vapor from ocean to land, causing additional rainfall there and helping to supply water for human activities. Besides circulation due to phase transition and vapor or liquid transport, H_2O molecules participate in photosynthesis reactions. If a stoichiometric molar ratio H_2O/CO_2 of 0.8 (as for cellulose, Sect. 3.4) and global carbon flows involved in photosynthesis of 123 Gt a^{-1} carbon (gross productivity GPP, Fig. 4.1) are assumed, resulting global H_2O flows reacting in photosynthesis are 148 Gt a^{-1}. This is only a minor fraction of the condensation/rainfall flows, reflecting the large amounts of H_2O required for physical processes in photosynthesis (e.g. transpiration, transport of trace elements).

The formal residence times or characteristic time scales resulting from H_2O inventories and flows are 3200 years for the ocean and 10 days for the atmosphere. Due to the small inventories in the atmosphere and the large flows caused by evapo-

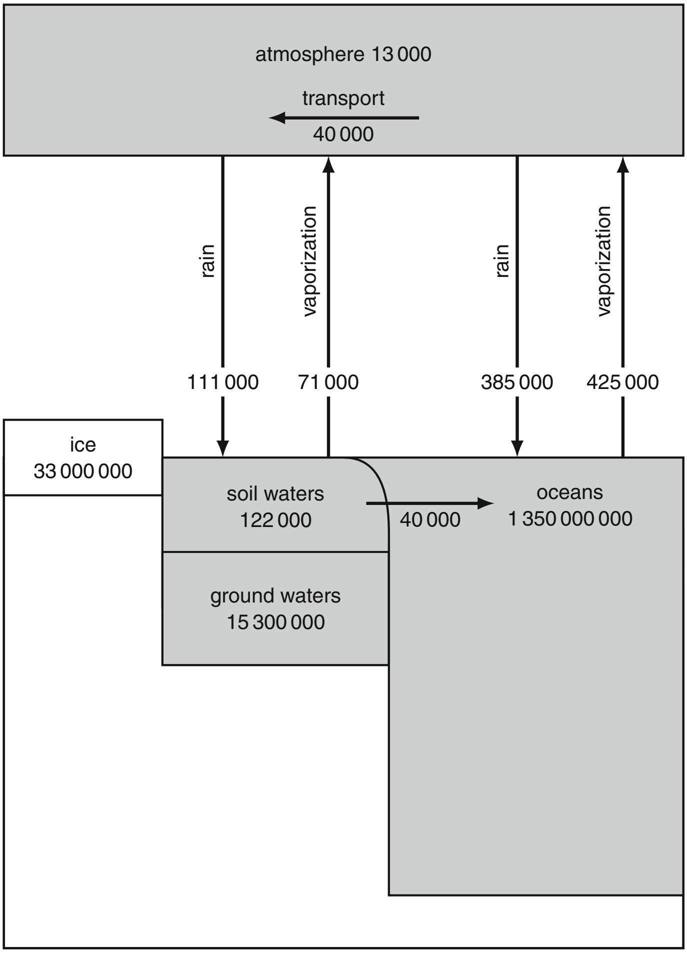


Fig. 4.4 H_2O reservoirs and annual global flows in Gt or Gt a^{-1} as average values, data from Schlesinger (1997)

ration/condensation, H_2O molecules remain only a few days as an average in the atmosphere (not considering a wide distribution of residence times due to slow vertical mixing in the atmosphere). Also in the ocean, slow vertical mixing characteristics cause a wide distribution of residence times.

Spatial Distribution of Precipitation

Global flow values of precipitation in Fig. 4.4 lead to an average yearly rainfall of 970 mm a^{-1} (for the total Earth surface of 5.1×10^8 km^2) according to Schönwiese (2008), Hupfer and Kuttler (2005). The corresponding value for land surface is 725 mm a^{-1}, with 30 % land surface of the Earth assumed. Spatial variability is in the range of near zero to about 15 000 mm a^{-1} and for Germany as an example country with temperate climate between 350 and 2500 mm a^{-1}.

The total amounts of precipitation on land surface can be – for mass balance purposes – divided into the fraction that is evaporated and the fraction that remains liquid (*run-off*). The latter is a limiting factor for biomass (i.e. food) production. As a global average, about 34 % of the global precipitation (equivalent to 244 mm a^{-1}) are available as run-off, corresponding to a flow of 40 000 Gt a^{-1} (Zehnder 2001). For agriculture and food production, about 20–35 % of this flow is estimated to be available, as a limitation for global food production (see below). In Germany, an industrialized example country with relatively large water resources, values for average precipitation/run-off are 840/350 mm a^{-1}. The latter represents a per-capita value of 1521 t cap^{-1} a^{-1}, of which about 3 % is distributed and consumed via public water supply networks.

As part of the global distribution of precipitation and run-off, Fig. 4.5 shows values for the Northern Hemisphere, as average for all longitudes. Moving from the equator to the north, a water-rich region (tropical zone) changes to a water-poor region (with a combination of arid and humid zones). In desert areas, nearly the total amount

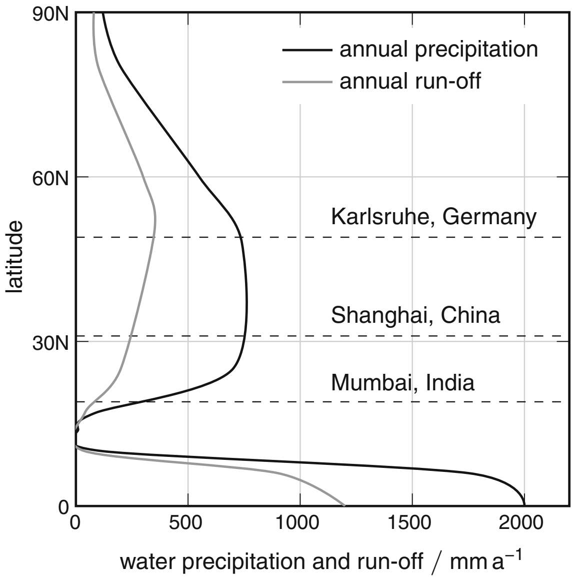


Fig. 4.5 Spatial variability of annual precipitation and water run-off in the Northern Hemisphere, data from Hupfer and Kuttler (2005) and Schultz (2000), see example locations in Table 3.2

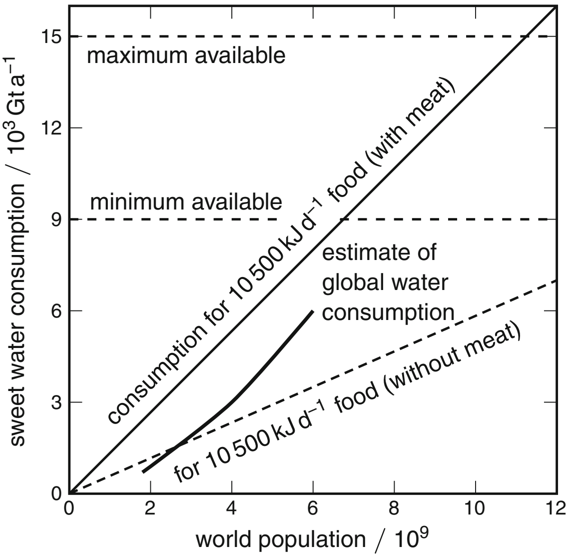
of precipitation is evaporated. Further north, there are again humid regions with sufficient run-off waters to grow agricultural crops for food supply.

Water Availability and Vegetation

Biomass growth by photosynthesis is directly linked to the availability of water (Larcher 2003, see Sect. 3.4). In temperate climate regions – such as Western Europe – growth of 1 kg biomass dry organic matter is linked to an integral amount of liquid water in the range of 250–1000 kg. Major fractions of this water contribute to temperature control mechanisms (by evaporation) and to the transport of trace elements into the biomass as dissolved ions. Correlations of large-area averages of net primary photosynthetic productivity (*NPP*) with annual precipitation and other external factors indicate that maximum food crop production is limited in many locations by the available amounts of water (Eqs. (3.14) and (3.15) and Fig. 3.13).

Figure 4.6 shows estimates of global water requirements for feeding human populations today and in the future (Zehnder 2001). Available water quantities are assumed to be in the range of 9000–15 000 Gt a^{-1}, which is equivalent to 22–38 % of the annual run-off or 8–14 % of the annual precipitation, both for the Earth's land surface. Water demands for growing 1 kg of carbohydrate plants and for producing 1 kg of meat (by feeding animals with carbohydrate biomass) are assumed as 1000 and 5000 L, respectively. It can be concluded that the biogeosphere can feed current and future human populations easily without excessive consumption of meat. With higher demand for meat, however, a total future population of 8, 9 or 10 billion human beings may have difficulties to produce enough food to survive.

Fig. 4.6 Correlation of sweet water consumption for food production and world population, after Zehnder (2001)



As local availability of water for food crop production is not evenly distributed, food export/import are commonly practiced today. In these cases, the term *virtual water* is used to quantify the amounts of water associated with the growth/production of the food exported/imported.

Present Changes in Global Water Cycle

Since the times of their first settlements, human communities have always tried to make use of the hydrologic cycle in order to supply sufficient water for their needs. Wells, drainage systems and piping networks for agricultural irrigation were built in early communities, followed later by dams for storage-lakes and other complex infrastructure edifices. The fall or decline of early civilizations could be caused by a loss of an adequate water supply. Today, due to a lack of water, large, potentially prosperous regions of Africa, Asia, Australia and South America, lying in the subtropical latitudes, are sparsely populated.

In most recent times, changes in the global water cycle can be observed that may be attributed to changes in the Earth's energy system, i.e. to rising temperature due to increasing greenhouse gas concentrations in the atmosphere. Examples of changes in the water cycle are (IPCC 2013a):

a) Total mass of solid H_2O is decreasing due to increased melting of glaciers, ice caps and the Greenland and Antarctic ice sheets.
b) Global mean sea levels are rising. During the 20th century, the average rate was (1.7 ± 0.5) mm a^{-1}. Sea level change is highly non-uniform spatially. In some regions, rates are up to several times the global mean rise, while in other regions sea level is falling. Sea level increases are caused by thermal expansion (about 50 %) and by the mass loss of glaciers and the land-based ice sheets.
c) Spatial and time variability of precipitation and surface fluxes is changing. Heavy rainfalls more often cause flooding, and desertification can be observed in other regions.
d) Ground water levels are falling if in high local concentrations of human populations (like in today's mega-cities) water consumption is not constantly replenished by natural fluxes.

4.4 The Nitrogen Cycle

Figure 4.7 depicts the complex global nitrogen cycle showing the interactions between the atmosphere, the land and the ocean. Some 80 % of Earth's total nitrogen is contained in the atmosphere (Galloway 2005), the largest of its reservoirs with about 3.87×10^9 Gt. N_2 is a very stable molecule that undergoes chemical reactions only with low rate or under severe conditions. Microorganisms have developed enzymatic processes to convert molecular nitrogen to ammonia (*nitrogen fixation*). NH_3 or NH_4^+ are then assimilated by organisms and converted into organic nitrogen components. Inorganic ammonium is also oxidized by microorganisms to nitrate that can be equally incorporated into biomass. High-temperature oxidation of N_2 to NO in lightnings and subsequent oxidation and precipitation as nitrate is another way of natural nitrogen fixation. The natural nitrogen cycle is completed by denitrification, the biological process that converts nitrate together with organic carbon back to N_2, carbon dioxide and water.

While the ocean mainly contains physically dissolved molecular nitrogen and only a relatively minor amount of organic nitrogen, land soils and biota are a major nitrogen reservoir. Nevertheless, Liebig recognized in the 19th century that the growing demand for food containing organic nitrogen as an essential nutrient would soon exceed the natural sources (Galloway and Cowling 2002). While the use of South

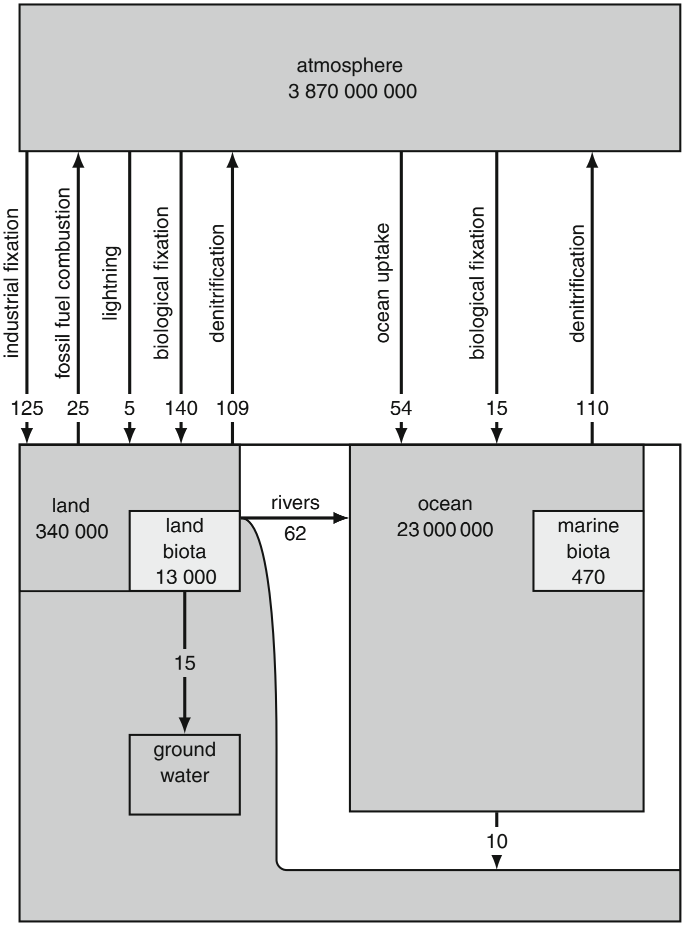


Fig. 4.7 Reservoirs and annual global flows of nitrogen in Mt or Mt a^{-1}, data from Schlesinger (1997), Jacobson et al. (2000), Schlesinger (2009), similar values given by Gruber and Galloway (2008) except for higher biological flows from and to ocean

American guano and nitrate deposits as fertilizers provided a temporary partial relief, subsequent effort was targeted at means for artificial nitrogen conversion. The first processes used the nitrogen contained in coal and the reaction of calcium carbide with atmospheric nitrogen to produce ammonia. However, the breakthrough for industrial nitrogen fixation required significant progress in catalysis, chemical reaction engineering, and high-pressure technology. In 1909, Haber demonstrated that nitrogen and hydrogen can be converted to ammonia under pressure and at elevated temperature in the presence of a solid catalyst:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3. \tag{4.2}$$

Only four years later, the first commercial ammonia synthesis plant started operation at the Ludwigshafen site of BASF AG in Germany. Although initially most of the production was used for German munitions during World War I, the Haber–Bosch process later became a virtually unlimited supply of reactive nitrogen that could be used to produce fertilizers which enhance food growth. Especially after 1950, ammonia from the Haber–Bosch process grew exponentially (see Fig. 4.8) to cope with the strong increase of the World Population (see Sect. 2.2.5). It has been estimated that more than half of the World Population is now dependent on nitrogen fertilizers from ammonia synthesis (Smil 2001). Despite continuous improvement over many decades, the Haber–Bosch process is still energy-intensive and requires a thermodynamic minimum of 18.6 GJ t^{-1} NH_3 (calculated as *LHV*, cf. Table 1.5). If one assumes that real plants on average require about twice this minimum value (Tavares et al. 2013), the 2013 ammonia production (174 Mt) corresponds to an energy demand of some 205 GW or 1.2 % of the global primary energy demand (cf. Fig. 5.10). Given the overwhelming importance of nitrogen fixation through ammonia synthesis, this appears to be a quite moderate contribution.

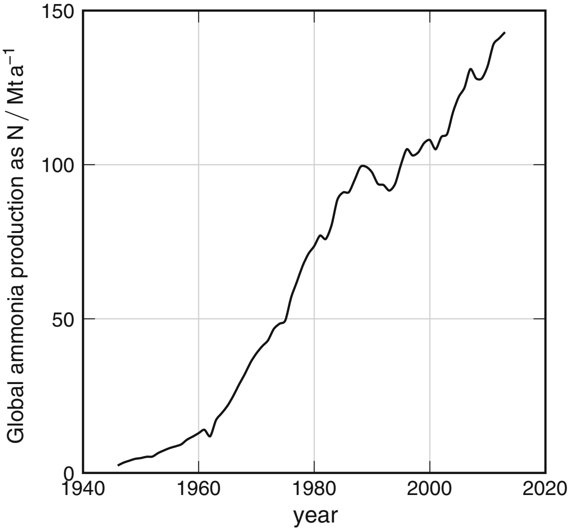


Fig. 4.8 Historical development of ammonia production (U.S. Geological Survey 2014)

Figure 4.7 shows that today industrial nitrogen fixation already has the same order of magnitude as biological fixation. Moreover, a flow of 25 $\mathrm{Mt\,a^{-1}}$ of nitrogen is emitted as nitrogen oxides to the atmosphere during fossil fuel combustion. Human activities have a significant impact on the global nitrogen cycle for other reasons. The use of reactive nitrogen as fertilizer leads to enhanced denitrification, nitrogen flow to the ocean from rivers, and nitrogen storage in ground waters. The net amount of organic nitrogen stored on land and in the ocean increases, as a closer inspection of the sum of all incoming and outgoing flows reveals.

Although industrial nitrogen fixation through the Haber–Bosch process will continue to play a vital role in order to secure the food supply for the growing World Population, there are several substantial negative impacts that must be taken into account (Galloway and Cowling 2002). Firstly, nitrogen oxides emitted during industrial combustion processes participate in acid rain and tropospheric ozone formation, an environmental problem that has already been resolved to some extent by application of modern abatement technologies such as the catalytic converter in automobiles. Secondly, enhanced nitrate flows to groundwater and aquatic ecosystems give rise to eutrophication and habitat degradation, especially in coastal waters. Thirdly, a small fraction of the products of the now strongly enhanced nitrification and denitrification is released to the atmosphere as N_2O. It is believed that most of the presently observed increase of atmospheric N_2O concentration can be attributed to the anthropogenic amplification of these natural processes. There are major concerns related to dinitrogen oxide due to its role as a potent greenhouse gas (cf. Table 3.1) and the contribution to stratospheric ozone depletion through catalytic action (see Sect. 4.7). An enhanced industrial nitrogen fixation can be expected for the next decades given the rising World Population. Thus it will be of utmost importance to find ways for even better control of nitrogen oxides emissions from combustion processes and especially for improvement of nitrogen efficiency during food production.

4.5 The Sulfur Cycle

The largest sulfur reservoirs are the sediments (7.44×10^9 Mt) and the ocean (1.28×10^9 Mt) whereas the atmosphere contains only a small amount of 2.8 Mt (see Fig. 4.9). Most of the sulfur in the ocean is present as sulfate (SO_4^{2-}), while the sediments contain both sulfate deposits (evaporites), mainly gypsum, and sulfides with FeS_2 (pyrite) being the most important species. Over geologic times, sulfates and sulfides are in balance coupled through deposition, weathering and, most importantly, the biological reduction of sulfates to sulfide sediments (Brimblecombe 2005, see also Sect. 4.8). Sulfate can also be assimilated by organisms and incorporated as organic sulfur, which is an essential constituent of proteins. However, the global amount of biologically fixed sulfur is relatively small.

There are significant flows to and from the atmosphere comparable to the global nitrogen cycle (see Fig. 4.7). Natural atmospheric sulfur flows comprise the formation of sulfate containing seaspray, which redeposits rather quickly, volcanic emissions

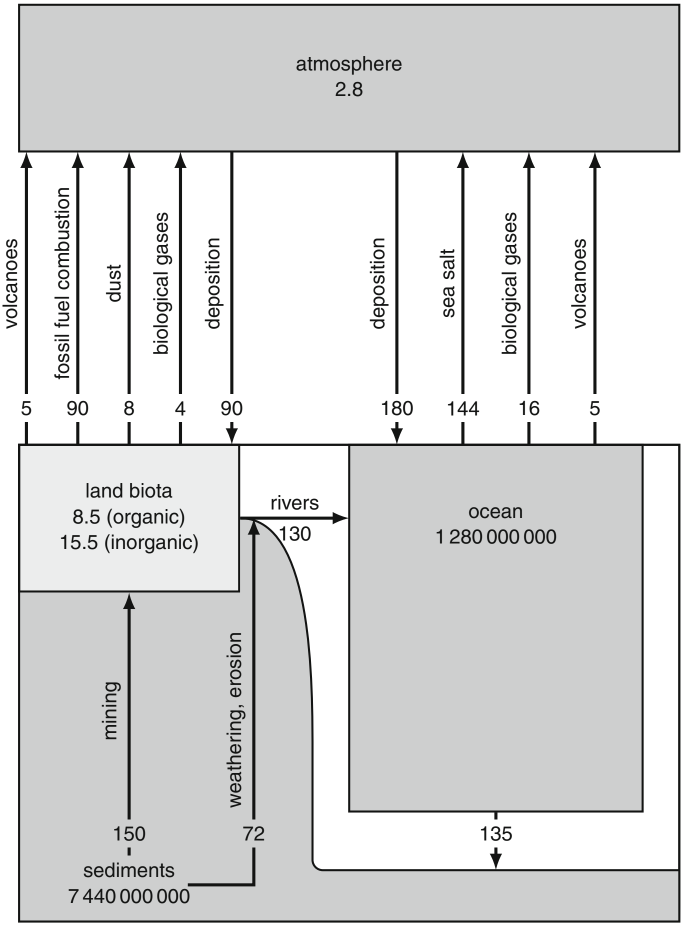


Fig. 4.9 Reservoirs and annual global flows of sulfur in Mt or Mt a^{-1}, data from Schlesinger (1997)

containing mainly SO_2 (and H_2S to a lesser extent), as well as the formation of biogenic gases such as carbonyl sulfide (COS) and dimethyl sulfide ($(CH_3)_2S$). Most of these components are rather short-lived as they undergo oxidation reactions followed by precipitation. The only exception is carbonyl sulfide with an atmospheric residence time of 25 a (see Table 2.5) that is able to reach the stratosphere because of the slow reaction rate with the OH radical. Dimethyl sulfide, on the other hand, is quickly oxidized and plays an important role in the production of sulfuric acid droplets that can act as cloud condensation nuclei. Since cloud formation leads to an increase of the albedo and results in lower surface temperatures diminishing biologic activity, dimethyl sulfide formation is an example of negative feedback and the stabilizing action of the biosphere (Charlson et al. 1987). Periods of intense volcanic activity may also result in strongly enhanced sulfate aerosol quantities and subsequent cooling of the troposphere for several years (Brimblecombe 2005).

Human impact on the sulfur cycle is as tremendous as it is on other global cycles. The most important example is the combustion of fossil fuels that results in sulfur dioxide emissions of about $90\,\mathrm{Mt\,a}^{-1}$. The atmospheric oxidation of this species gives rise to acid rain formation, an air pollution problem that has lead to massive damage to lakes and woods, especially in Europe and North America. However, as the mean residence time of this reactive component is only a few days, acid rain is restricted to a range of approx. 1000 km around the industrial sources. In the late twentieth century, effective methods such as the scrubbing of stack gases with limestone ($CaCO_3$) slurries have already lead to a strong decline of sulfur dioxide emissions in industrialized economies. It can be expected that developing countries will implement similar abatement technologies and that sulfur dioxide emissions from anthropogenic sources will decrease significantly during the twenty-first century. Another anthropogenic impact on the global sulfur cycle is associated with the production of sulfuric acid, one of the most important base chemicals with a world production capacity of about $150\,\mathrm{Mt\,a}^{-1}$. Sulfuric acid is manufactured from elemental sulfur, either obtained from natural deposits or through the Claus process using the reaction of H_2S with SO_2, and used for a variety of further reactions the most important of which is the production of sulfates for the fertilizer industry. Agriculture and other industrial activities are responsible for roughly doubling the natural sulfur load of rivers. Given the high sulfate concentration of seawater, this is not a major environmental concern as long as only sulfate and no significant amounts of organic sulfur components are released to river waters.

4.6 The Phosphorus Cycle

Phosphorus is essential to life as it plays key roles during biochemical reactions involving genetic material (RNA, DNA) and energy transfer (adenosine triphosphate, ATP). It is moreover contained as phospholipids in organic membranes and as hydroxyapatite in bones (Ruttenberg 2005). A unique feature of the global phosphorus cycle (Fig. 4.10) is the fact that it has no major gaseous component. The very small atmospheric amount of 3 kt consists only of phosphate containing aerosols as no gaseous phosphorus species is stable under the oxidizing atmospheric conditions.

The sediments contain large amounts (4×10^9 Mt) of phosphorus as apatite minerals $Ca_{10}(PO_4)_6(X)_2$ where X may be OH, F, Cl or mixtures thereof. Weathering of these minerals leads to the formation of soluble components that can be taken up by plants. However, the availability of soluble phosphorus is often extremely low due to strong adsorption at various soil constituents. For these reasons, land plants have developed efficient strategies to recycle organically bound phosphorus and to minimize any losses. Land biota contain about 3000 Mt phosphorus with a residence time of about 16 a. Transport of phosphorus from land to the ocean occurs mainly in rivers whereas the deposition of atmospheric aerosols is of lesser importance. The ocean contains an overall amount of 90 Gt phosphorus as soluble phosphate

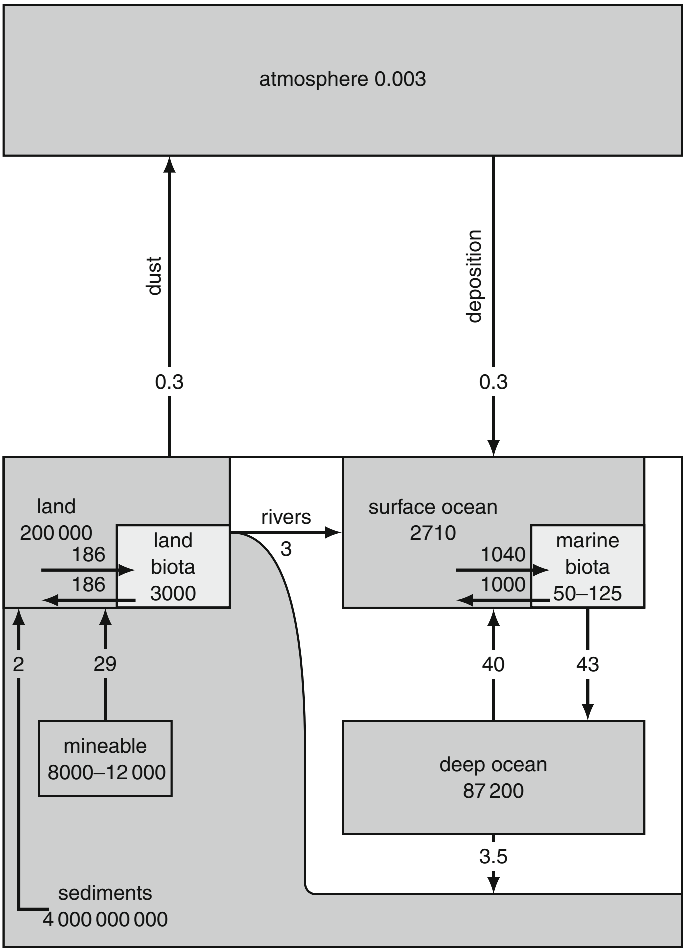


Fig. 4.10 Reservoirs and annual global flows of phosphorus in Mt or Mt a^{-1}, after Jacobson et al. (2000), simplified, flow in phosphate mining: 2012 (Pinnekamp et al. 2013), resources: see Sect. 6.1.2

around 3 % of which is available for marine biota. Despite the relatively low organic phosphorus reservoir in the surface ocean (50–125 Mt), the exchange between marine biomass and ocean is rather fast with a residence time of only 2–6 weeks. Transport of phosphate to the deep ocean and subsequent sedimentation closes the global P cycle.

Human impacts on the phosphorus cycle are mainly related to mining of phosphate containing ore for uses in industry and especially as agricultural fertilizer. Part of this anthropogenic phosphorus flow of 29 Mt a^{-1} (2012) cannot be taken up by plants. This leads – together with increased erosion, deforestation and waste disposal – to a strongly enhanced phosphorus load in the rivers (Ruttenberg 2005). Similar to the anthropogenic change of the nitrogen cycle (Sect. 4.4), this has often lead to eutrophication in lakes and the coastal ocean with detrimental effects for these ecosystems. Moreover, strongly increasing demands of phosphates for fertilizer production may lead to a shortage in the future (Gilbert 2009), although estimated values of resources have recently increased (see Sect. 6.1.2). Recycling of phosphorus from waste water with innovative technologies will lower the flow of raw material consumption.

4.7 The Chlorine Cycle

Although chlorine is not among the most prominent constituents of the Earth crust (cf. Table 2.3), its global biogeochemical cycle as well as the alterations caused by human activities are highly interesting and will be treated in some detail in this section.

Reservoirs

Figure 4.11 reveals that the major reservoirs of chlorine are the sediments (60×10^9 Mt), the ocean (26×10^9 Mt) and the land (24×10^3 Mt), whereas the atmosphere contains only relatively minor amounts (5.7 Mt). The ocean reservoir consists of dissolved ionic chlorides. The soil and the sediments, on the other hand, mainly contain soluble minerals such as sodium chloride. In the atmosphere, gaseous chlorine (4.7 Mt) exists as HCl and CH_3Cl, however, the hydrogen chloride fraction (0.4 Mt) is small due to its high reactivity. As methyl chloride is relatively stable with an atmospheric residence time of 1 a (Table 2.5), it is able to reach the stratosphere. Here, it participates in complex photo-induced reactions. The great importance of these reactions for the stratospheric ozone layer and especially the role of anthropogenic chlorine emissions will be discussed later. In addition to the gaseous species, the atmosphere also contains about 1 Mt of sea salt aerosols, which is transported only at low atmospheric altitudes and redeposits rather quickly.

Processes (Natural and Anthropogenic)

By far the largest flux from any chlorine reservoir is the generation of sea salt aerosols through waves in the marine boundary layer. However, 99.9 % of these aerosols readily return to the ocean surface by wet and dry deposition. A small fraction of the chloride aerosols is transformed to gaseous chlorine compounds. Hydrogen chloride is the main product of these reactions while even more reactive gases such as Cl_2, HOCl and $ClNO_2$ are formed to a much lesser extent (Graedel and Keene 1996). Oceanic biomass is also emitting about 2 Mt a^{-1} chlorine as methyl chloride. Terrestrial ecosystems contribute a further 0.5 Mt a^{-1} CH_3Cl. This value is summarized in

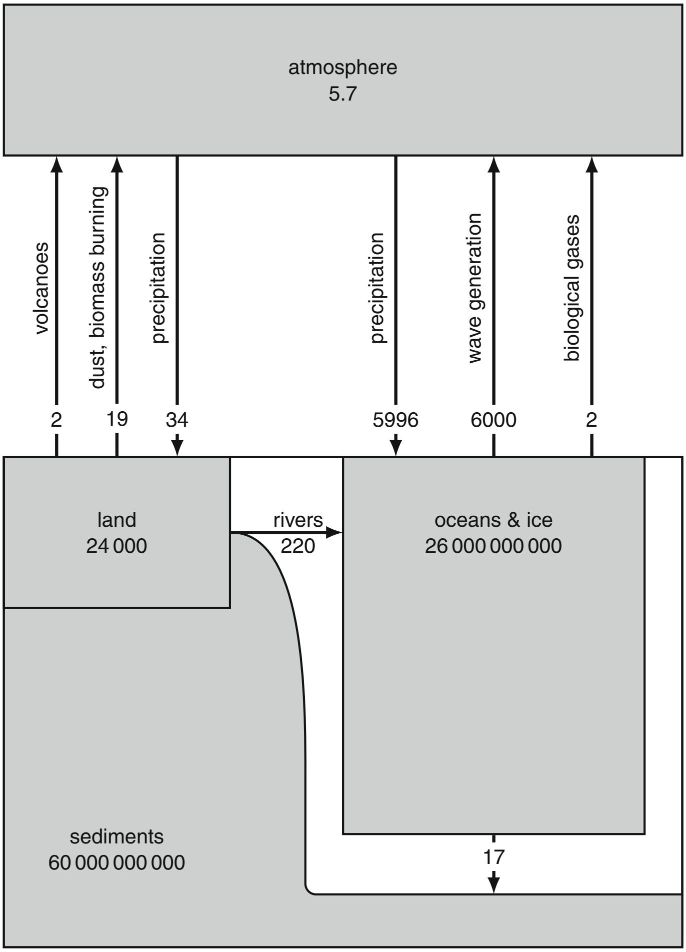


Fig. 4.11 Reservoirs and annual global flows of chlorine in Mt or Mt a^{-1}, after Graedel and Keene (1996), simplified

Fig. 4.11 together with the amounts of CH_3Cl emitted from land to atmosphere by biomass burning (3 Mt a^{-1}) and through mineral aerosols produced by wind in dry areas (15 Mt a^{-1}). In the reverse direction, there is a continuous chlorine flow by wet (rainfall) and dry (aerosols) deposition with a sum of about 34 Mt a^{-1}. Volcanoes are an additional source for atmospheric chlorine with 2 Mt a^{-1}, mainly in form of HCl. Finally, there is a large flow of dissolved ionic chlorine from land to ocean (220 Mt a^{-1}) in rivers whereas some 17 Mt a^{-1} of oceanic chlorine are deposited to the sediments. The apparent imbalance of the ocean inputs and outputs results in a slow increase of chloride concentration.

Except for the production of methyl chloride, the role of organisms in the biogeochemical chlorine cycle and the amounts of natural organically bound chlorine has been underestimated until recently (Öberg 2002). There is growing evidence that various forms of biotic processes drive the formation of organic chlorine components in soil. The resulting amount of organically bound chlorine may even exceed the corresponding amount of chloride. It appears that chlorine has a vital role in organisms and ecosystems not only in its ionic form but also as a broad variety of organochlorine components, the function of which is in many cases unknown.

Chlorine is one of the most important base chemicals with a worldwide production capacity of more than $50\,\mathrm{Mt\,a^{-1}}$ (O'Brien et al. 2005). Industrial chlorine production has been developed in the last decade of the 19th century and has been of high economic importance since then. Elemental chlorine (Cl_2) is manufactured together with sodium hydroxide and hydrogen by electrolytic splitting of sodium chloride solutions in the so-called chlor-alkali electrolysis. The highly reactive chlorine is further processed primarily to chlorine containing polymers (e.g. polyvinyl chloride, PVC) or it acts as an intermediate reactant during the production of important chlorine-free polymers such as polyurethanes or polycarbonates. In the latter case, chlorine is being recycled to an increasing extent. Further applications of chlorine comprise the manufacture of a broad variety of organic chlorine compounds which are used as solvents, pesticides, or disinfectants. Older chlorine production processes used large amounts of toxic mercury and evoked strong environmental concerns caused by mercury emissions. However, the emission situation has been greatly improved during the last decades. Moreover, new environmentally benign chlor-alkali processes have been developed and recent research efforts are targeted at a further significant reduction of electrical energy demand (Moussallem et al. 2008). Thus, it appears that chlorine production itself is on the way to environmental acceptability. Unfortunately, several industrial chlorine containing products continue to be great threats to human health and the environment. These components will be discussed in the following sections.

Persistent Organic Pollutants: The Dirty Dozen

Persistent organic pollutants (POPs) are organic components with strong resistance to environmental degradation by chemical, photochemical or biological processes. These compounds are consequently capable of long-range transport and tend to accumulate in animal and human tissue. Among these POPs are several polychlorinated components that have been used extensively in the last decades as pesticides, fungicides, insecticides or for other industrial purposes. One prominent example is DDT (dichlorodiphenyltrichloroethane), a well-known pesticide that became famous after World War II for its high efficiency during the control of mosquitoes spreading malaria. A second important class of persistent organic components with highly detrimental properties are polychlorinated dibenzodioxins (PCDDs) and -furans (PCDFs). Components with chlorine in the 2, 3, 7 and 8 position of the molecules are extremely toxic, teratogenic and carcinogenic. PCDDs and PCDFs became first known as contaminants in Agent Orange, a herbicide used in the Vietnam War and later during the Seveso accident in a chemical plant in Northern Italy in 1976. In 2001 the Stockholm Convention on Persistent Organic Pollutants was signed, where the parties agreed to a political process by which POPs should be reduced or eliminated. The 2001 POP list contained twelve distinct chemical components commonly called the Dirty Dozen. All of these components are synthetic polychlorinated organic substances.

CFCs and Stratospheric Ozone Depletion

Chlorofluorocarbons (CFCs) are halogenated hydrocarbons developed in the 1930s as non-toxic and non-flammable components for purposes such as refrigerants, solvents, aerosol-spray propellants and foam-blowing agents. These convenient materials, e.g. trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12) found widespread application after World War II. Given their long lifetime of up to 100 a (cf. Table 2.5), CFCs accumulate in the atmosphere and eventually reach the stratosphere. CFCs are not only among the most important greenhouse gases (see Sect. 3.2) but have also a deleterious effect on the stratospheric ozone layer, that shields organisms on Earth from harmful effects of ultraviolet radiation. In the mid-seventies Rowland and Molina (1974) predicted that chlorine atoms formed by photochemical breakage of CFC molecules lead to a decrease of the stratospheric ozone levels by catalytic action. However, measurements of Antarctic ozone concentrations did not show a significant reduction until the early 1980s. Thus, corrective political action came too late to prevent the *ozone hole* over the Antarctic. Figure 4.12 shows that ozone concentrations especially in the Antarctic winter (October) drop dramatically and that average values are much lower than the normal ca. 300 DU.

The reason is that the stratospheric chlorine concentration (Fig. 4.13) had already in 1980 been multiplied by a factor of four, from 0.55 ppb – the pre-industrial value linked to methyl chloride emissions by the ocean (Dong et al. 2003) – to around 2 ppb. After the unambiguous verification of the ozone depletion process (Farman et al. 1985), it became evident that the production of CFCs and related substances had to be phased out as soon as possible. In 1987 the Montreal Protocol on Substances that Deplete the Ozone Layer was signed. This protocol has been subsequently tightened on several additional international meetings. Today, all member countries in the United Nations have ratified the Montreal Protocol and the world production of CFC has been drastically reduced. It is now generally expected that the stratospheric chlorine concentrations will soon start to decrease and that 1980 levels could be reached approximately around 2050 provided that no future growth of other ozone-depleting trace gases such as N_2O takes place (Weatherhead and Andersen 2006).

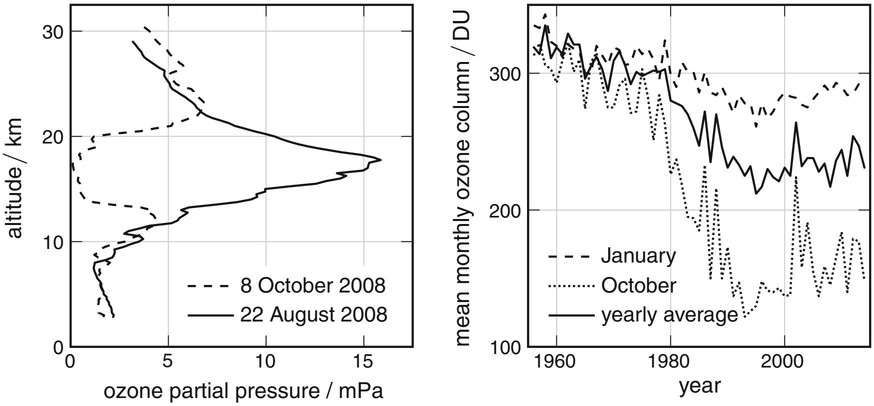


Fig. 4.12 Vertical ozone profiles over South Pole (*left*) (data: http://www.esrl.noaa.gov/gmd/dv/ftpdata.html) and mean values for October, January and yearly ozone column (*right*) over Antarctic Halley Bay station (76S) (DU: Dobson unit (column of 0.01 mm pure ozone at 0 °C and 1 atm), data: https://legacy.bas.ac.uk/met/jds/ozone/data)

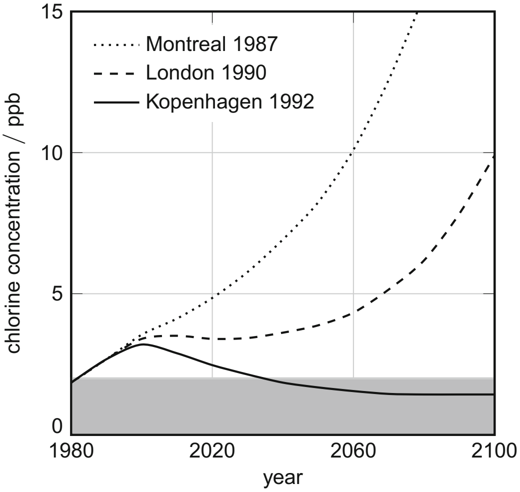


Fig. 4.13 Predicted development of stratospheric chlorine concentrations after implementation of emission reduction measures according to the Montreal Protocol and subsequent tightening of the agreement made in London and Kopenhagen, data after Tabazadeh and Cordero (2004), *gray* noncritical levels

Conclusion

Chlorine is abundant in nature and is – at least as chloride ion, but possibly also as natural organochlorine components – necessary to most forms of life. It is furthermore a large-scale industrial base chemical required for the production of important polymeric materials. On the other hand, several synthetic chlorinated organic substances have extremely harmful effects to human health, ecosystems and the Earth system as a whole. Fortunately, these components and their effects have been recognized and counteractive measures have been started. The Stockholm Convention on Persistent Organic Pollutants and especially the Montreal Protocol on Substances Depleting the Ozone Layer are success stories that will lead to a responsible usage of chlorinated substances in the future. Due to the widespread adoption of the Montreal Protocol one can expect that the *ozone hole* will cease within a few decades and that important greenhouse gases can be significantly reduced. It is thus a positive example of international co-operation with Kofi Annan, the former Secretary General of the United Nations, saying in 2003 that *perhaps the single most successful international agreement to date has been the Montreal Protocol* (http://www.ozone.unep.org).

4.8 Interaction of Material Cycles

The global material cycles described in the previous sections are not independent of each other. An obvious example is the coupling of the carbon and oxygen cycles by photosynthesis (React. (3.12)) and respiration, i.e. oxidation of the organic matter with O_2 to carbon dioxide and water. If the average initial composition of the biomass formed during photosynthesis is summarized with CH_2O, the interaction of these two processes can be described in a very simplified form with the following stoichiometry of a reversible reaction.

$$CO_2 + H_2O \rightleftharpoons O_2 + CH_2O \tag{4.3}$$

Here, CH_2O is not formaldehyde but the average composition of a typical carbohydrate. Although biomass undergoes reductive processes after burial in the sediments leading to a loss of oxygen and hydrogen (cf. Fig. 5.21), this simplified stoichiometry is generally applied to models of biogeochemical cycles (Petsch 2005). React. (4.3) explains how a constant atmospheric oxygen concentration is maintained at equal rates of photosynthesis and respiration. If respiration does not consume all organic matter produced by photosynthesis, accumulation of oxygen in the atmosphere is accompanied by an increase of organic carbon components in the sediments as it has occurred intensively during earlier phases of Earth history (see Fig. 2.4).

Garrels and Lerman (1981) have shown that sulfur plays a key role in the oxygen-carbon system and proposed an extended model. This interaction is caused by the fact that organic matter is oxidized during bacterial reduction of sulfate to sulfide resulting in the formation of carbon dioxide without consumption of O_2. The following overall stoichiometry (React. (4.4)) was proposed to explain the interactions of oxidized and reduced sulfur components and the different carbon species (carbon dioxide, carbonate and buried organic matter simplified as CH_2O). Figure 4.14 depicts the results of this model for a steady-state situation. The overall system of ocean and atmosphere contains dissolved sulfate (42×10^{12} mol) as well as carbonate and gaseous carbon dioxide with a sum of 3.3×10^{12} mol. This system is coupled

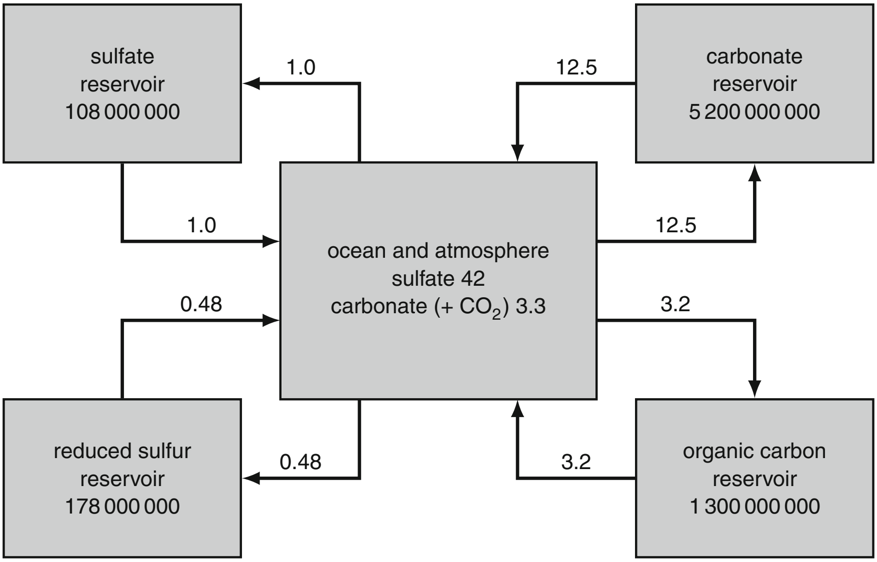


Fig. 4.14 Simple steady-state model of global sulfur and carbon cycles from Garrels and Lerman (1981), reservoirs in 10^{12} mol, flows in 10^{12} mol a^{-1}

by exchange flows to the sediments that contain the given amounts of organic carbon, carbonate rocks as well as sulfate minerals and sulfides (pyrite).

$$4\,FeS_2 + 8\,CaCO_3 + 7\,MgCO_3 + 7\,SiO_2 + 15\,H_2O \rightleftharpoons 15\,CH_2O + 8\,CaSO_4 + 2\,Fe_2O_3 + 7\,MgSiO_3 \quad (4.4)$$

The value of 1300×10^{18} mol organic carbon assumed by Garrels and Lerman (1981) corresponds to 15.6×10^{18} kg and is comparable to the amount of sedimentary carbon as depicted in Fig. 4.1. If the rates of the reversible React. (4.4) are not equal, the model predicts that during phases where organic carbon in the sediments increases, a corresponding increase of the sulfate reservoir takes place while the pyrite and carbonate reservoirs should decrease.

The coupling of the global cycles of carbon and nitrogen and the possible implications for the future development of the climate were discussed by Gruber and Galloway (2008). In all living organisms, especially in marine biota, the elemental C/N ratios are relatively constant. Anthropogenic acceleration of the global nitrogen cycle may therefore enhance the ability of land and marine biota to absorb at least part of the anthropogenic CO_2 emissions. However, it can be foreseen that nitrogen supply will be the limiting factor for enhanced photosynthesis if man-made carbon dioxide emissions continue to rise strongly. The ability of the biosphere to act as CO_2 sink will then be seriously affected.

In conclusion, it appears that a complete picture of the interactions of the biogeochemical cycles has not yet been developed. Further progress is required to include these material cycles in future and improved climate models (IPCC 2007).

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Chapter 5
Anthropogenic Material and Energy Flows

Given the characteristic features of the natural carbon cycle, anthropogenic CO_2 emissions related to the development of industrialization have caused significant changes in the composition of the atmosphere. In this chapter, the historical development of anthropogenic energy and carbon flows is presented, in the context of natural changes during the history of the Earth. The structure of the present German energy supply system serves as an example of industrialized countries, with primary energy source distribution, energy conversion and energy utilization sectors (mobility and transport, industry, buildings and domestic use). Fossil CO_2 emissions correlate with the selection of individual fossil fuels according to the stoichiometry of the chemical combustion reaction.

5.1 Changes in the Natural Carbon Cycle

During the Earth's history, there have been significant variations in the global carbon cycle, caused by natural factors (e.g. changes in surface temperature due to changes in solar irradiation). Given these natural changes, variations due to human activities and their causes are difficult to identify.

5.1.1 Overview of Factors and Phases

Changes in the global carbon cycle are of major significance as atmospheric concentrations of carbon-containing gases (CO_2, CH_4) affect absorption of long-wave radiation and the Earth's energy balance (see Chap. 3). Carbon-containing gases in the atmosphere thus contribute to the third of the three fundamental ways in which the Earth's radiation balance can change, thereby causing climate change (IPCC 2007a, p. 449): (i) changing the incoming solar radiation (e.g. by changes in the Earth's orbit or in the Sun itself), (ii) changing the fraction of solar radiation that is

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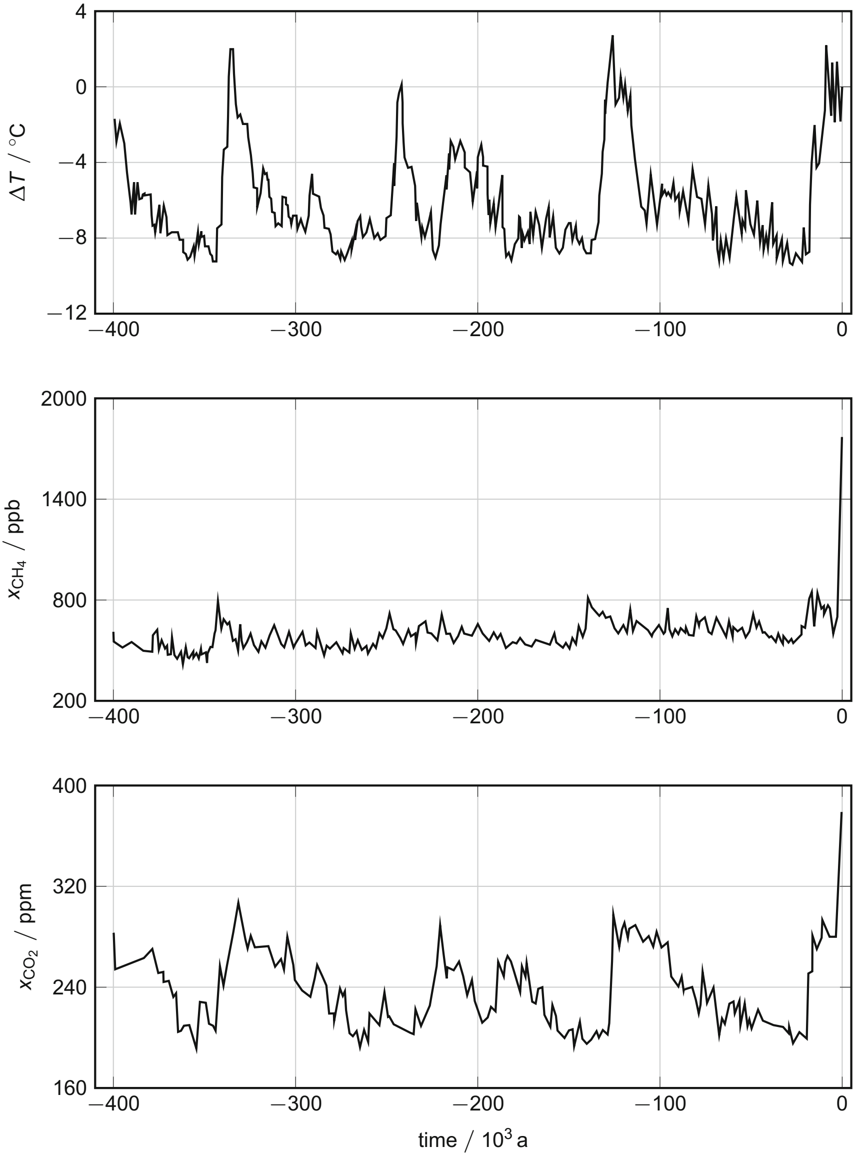


Fig. 5.1 History of temperature in Antarctica (relative to today) and atmospheric concentrations of CO_2 and CH_4, *source* IPCC (2007a, p. 444), Schönwiese (2008), Rahmstorf and Schellnhuber (2007), based on Petit (1999)

reflected (called albedo, being changed, for example, by changes in land cover, or atmospheric aerosol concentrations), and (iii) altering the long-wave energy radiated back to space due to changes in greenhouse gas concentrations. During the past 400 000 years there have been natural periodic variations (cycles) of atmospheric

CO_2/methane concentrations and average temperature on Earth with characteristic time constants (Fig. 5.1). These variations were discovered when ice core samples were retrieved from research stations in Antarctica, containing trapped bubbles of ancient air. The bubbles revealed the composition of the atmosphere at the time the ice layer was formed. Concentrations of CO_2 and methane together with temperature rose and fell in a regular pattern during the time period accessible (e.g. more than 400 000 years in Vostok). For example, 100 ka glacial-interglacial cycles of larger amplitudes can be seen. Other cycles show peak values every 22 000 years (for methane, with the highest production in wetlands when the Northern Summer coincides with the Earth's closest passage to the Sun, Ruddiman 2005a). Ice core records show that atmospheric CO_2 concentrations varied in the range 180–300 ppm and methane in the range 300–700 ppb over the glacial-interglacial cycles of the last 650 thousand years.

These cycles are caused by natural variations in the Earth's orbit and, as a consequence, changes in the distribution of sunlight intensity. The quantitative and mechanistic explanation of the CO_2 variations remains a topic in climate research (IPCC 2013; IPCC 2007a, p. 446). Most explanations propose that changes in oceanic processes are the cause for low glacial CO_2 concentrations. For example, CO_2 is more soluble in colder water than in warmer water, and therefore changes in surface and deep ocean temperature have the potential to alter the atmospheric CO_2 concentration.

Two different effects of human activities on the amounts of carbon-containing greenhouse gases stored in the atmosphere are presently debated. (i) It is common understanding today that human activities since the beginning of industrialization have contributed to changes in CO_2 level in the atmosphere of the Earth (see Sect. 4.1). According to the mass balance view, release of fossil carbon as the combustion product CO_2 into the atmosphere has increased the amount of carbon stored there, given the relatively slow exchange processes with other reservoirs (ocean, biosphere, sediments). (ii) A second effect of human activities on global climate was suggested in recent publications as a hypothesis, that started much earlier (Ruddiman (2005a, b), Fig. 5.2). According to this hypothesis, early settlements since the neolithic revolution about 10 000 years ago may have led to CO_2 and methane release into the atmosphere. These considerable greenhouse gas emissions may have been caused by clearing of forests, flooding of lowlands, and fermentative plant decomposition in wetlands.

In any case, alterations of the natural periodic behavior shown in Fig. 5.1 can be detected only with difficulty as superimposed variations, given the complex mechanisms involved. For example, the hypothesis of Ruddiman is based on modeling studies for the Northeastern Canadian Arctic. Suggested is a scenario where natural climate was warm 8000 years ago because of strong solar radiation in summer and high natural levels of greenhouse gases. Since that time, solar radiation levels have been falling in response to natural orbital changes causing a natural cooling. Within the last few thousand years, this cooling would have reached the threshold at which glaciation would have become possible unless humans had begun adding greenhouse gases to the atmosphere in amounts sufficient to keep the climate warm enough to avoid glaciation (see Sect. 5.1.2). The more recent effect during the industrial era, i.e. large-scale CO_2 emissions due to fossil fuel combustion, has led to significantly higher rates of climate variation.

5.1.2 Phase 10 000–250 Years Ago

The hypothesis by Ruddiman suggesting that glaciation was prevented by anthropogenic pre-industrial greenhouse gas emissions is controversial. For example, there is the argument that in earlier interglacials there also were long periods with relatively stable high CO_2 and CH_4 concentrations without any human effects active (IPCC 2007a, p. 460). It is also questionable if the carbon release by early anthropogenic land use could cause a carbon flow significant enough in quantity (IPCC 2007a, p. 460). In the context of the present discussion, the hypothesis by Ruddiman gave the inspiration for the simple carbon flow estimate as a plausibility check described in Box 5.1.

An example of local effects connected with early settlements is shown in Fig. 5.3 (Williams 2006, p. 49). In the tropical forest environment of the warm, well-watered Mexican Gulf lowlands, agricultural societies like the Classic Maya civilization flourished beginning at about 3000 years before present. The population rose steadily to

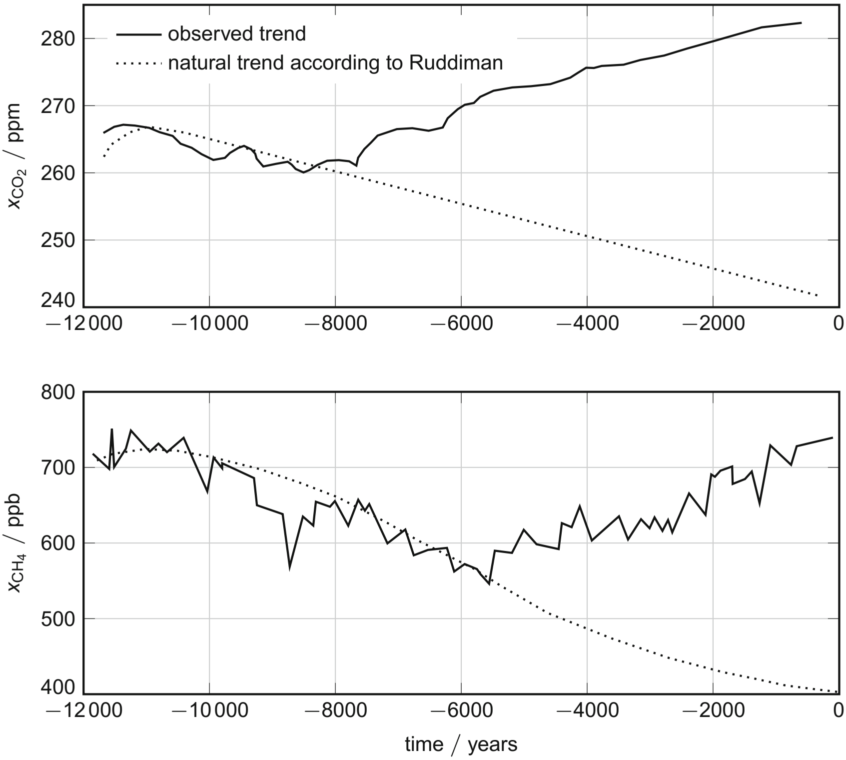


Fig. 5.2 Trends of atmospheric gas concentrations during phase 10 000–250 years ago, *top* CO_2 trend reversal after falling for 2500 years, possibly due to early agriculture and forest clearing, *bottom* CH_4 trend reversal after falling for 6000 years, due to flooding lowlands near rivers to grow rice in East Asia, after: Ruddiman (2005a, p. 50/51)

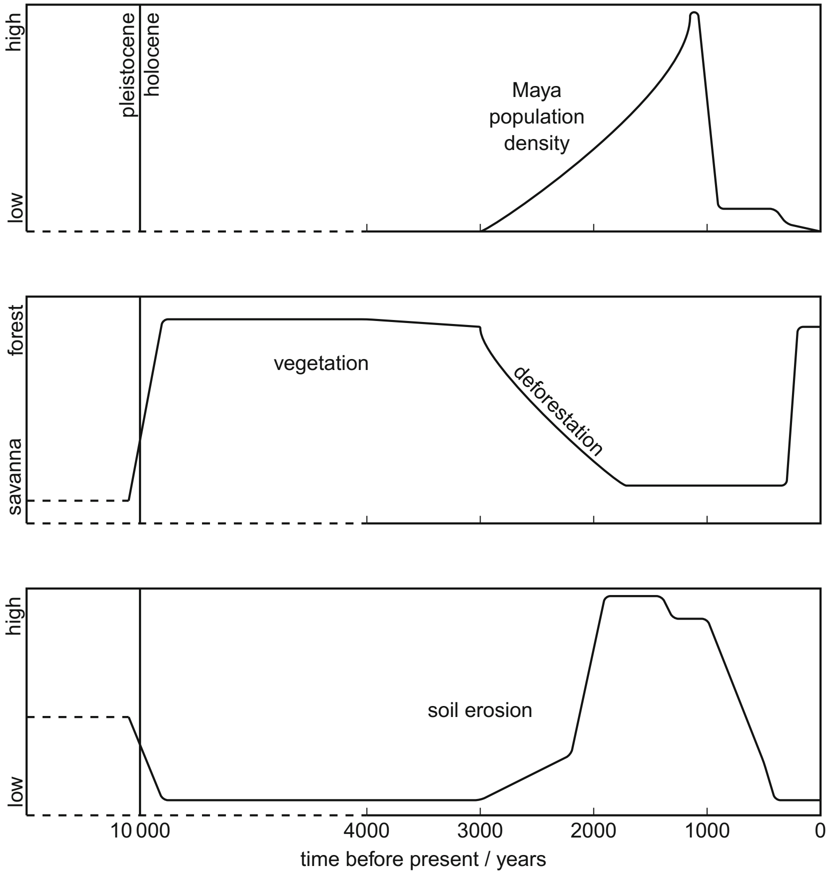


Fig. 5.3 History of population density, deforestation, and soil erosion during Maya settlement, 10 000–0 years before present, based on: Williams (2006), after Deevy et al. (1979)

reach a peak of between 2.6 and 3.4 million by the year 800 (i.e. 1200 before present), with a density of 117–151 persons per km^2. In the early ninth century the population collapsed abruptly, dropping to about 536 000 in the year 1000. The whole civilization was in disarray, for reasons related to limited food crop supply. As population increased between 1000 BCE and 800, deforestation increased, soil erosion accelerated, and essential nutrients such as phosphorus were leached out of the soils of this potentially fragile environment. Productivity must have declined significantly.

Box 5.1: Carbon Flows caused by Early Human Settlements

There was a global population of about 10 million humans 7000 years ago. If communities that formed and settled cut or burnt forests in the neighborhood, it can be assumed that a group of 100 humans cleared an area of 10 ha. With typical values for biomass (phytomass) amounts per area of $60\,\text{kg}\,\text{m}^{-2}$ (rainforest) and $30\,\text{kg}\,\text{m}^{-2}$ (temperate forest) and their distribution of 50/50 %, the following amounts of carbon released can be estimated as follows.

Total area cleared: $10 \times 10^6\,\text{ha} = 10 \times 10^{10}\,\text{m}^2$

Mass of vegetation burnt: $10 \times 10^{10} \times 45\,\text{m}^2 \times \text{kg}\,\text{m}^{-2}$

Carbon in biomass burnt: $0.45 \times 10^9 \times 0.5 = 0.225 \times 10^9\,\text{t} = 0.225\,\text{Gt}$

If this clearing of forest is assumed to have occurred within 10 years, a rate of carbon released into the atmosphere can be estimated:

$$F_{m,C} = 0.0225\,\text{Gt}\,\text{a}^{-1} \quad (\text{equivalent to } 0.0825\,\text{Gt}\,\text{a}^{-1}\ \text{CO}_2)$$

Looking at the global carbon cycle diagram in Sect. 4.1 (Fig. 4.2), this carbon flow appears rather small with respect to potential changes in the atmospheric carbon pool.

5.1.3 Phase 250 Years Ago Until Today

The industrial era began with the systematic use of coal as a densified form of chemical (fuel) energy. Technical innovations (such as the steam engine, and blast furnace) allowed for the generation of mechanical energy from coal, in addition to thermal energy, or for the production of metallurgical iron on industrial scale. Railway and steam-driven ships opened new options for transporting people and goods. The advantage of using coal instead of biomass (as in earlier times) lies in the higher energy density per mass or volume (see Sect. 5.5), a large supply potential for replacing biomass, and availability of very large amounts in one location (i.e. at the site of the coal mine).

Later, liquid and gaseous energy resources (petroleum and natural gas) were discovered, with advantages in handling and processing characteristics as compared to coal. Energy conversion processes are based on combustion with air according to stoichiometric equations given in Table 5.1, with higher heating values HHV that are higher than with biomass. The main combustion products are gaseous CO_2 and H_2O.

During the past 250 years, there was a continuous growth of fossil fuel applications. Resulting fossil CO_2 emissions according to reactions given in Table 5.1 increased in parallel, shown as carbon emissions in Fig. 5.4. It was not before 1900 that petroleum applications became significant while natural gas has contributed to global energy supply since about 1930. Shares of the individual energy resources reflect market criteria (availability, price) as well as strategic aspects of national economies. The energy applications of coal, petroleum, and natural gas involve huge mass flows which by far exceeded mass flows processed in the chemical or manufacturing industries. The total carbon emission around 2005 in Fig. 5.4 agrees with the value indicated in the global carbon cycle representation in Fig. 4.1 ($7.8\,\text{Gt}\,\text{a}^{-1}$).

Table 5.1 Stoichiometric equations and higher heating values for selected fuels

Fuel	Stoichiometry of combustion reaction	HHV/MJ kg^{-1}
Bituminous coal	$CH_{0.8}O_{0.1} + 1.15\,O_2 \rightarrow CO_2 + 0.4\,H_2O$	34.6
Lignite	$CH_{0.8}O_{0.3} + 1.05\,O_2 \rightarrow CO_2 + 0.4\,H_2O$	26.3
Petroleum	$CH_{1.8} + 1.45\,O_2 \rightarrow CO_2 + 0.9\,H_2O$	45.9
Natural gas	$CH_4 + 2.0\,O_2 \rightarrow CO_2 + 2.0\,H_2O$	55.7
Biomass	$CH_{1.6}O_{0.7} + 1.05\,O_2 \rightarrow CO_2 + 0.8\,H_2O$	19.6

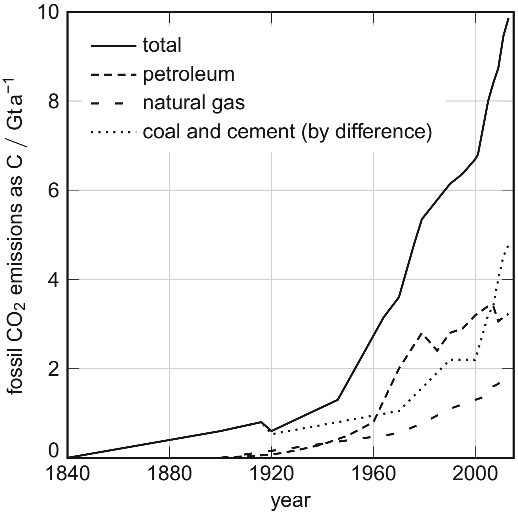


Fig. 5.4 History of CO_2 emissions (as carbon) from fossil fuel utilization, trends and selected data, *data sources* Schimel (2000), IPCC (2007a), Hiller and Kehrer (2000), BP (2014), CDIAC (2014)

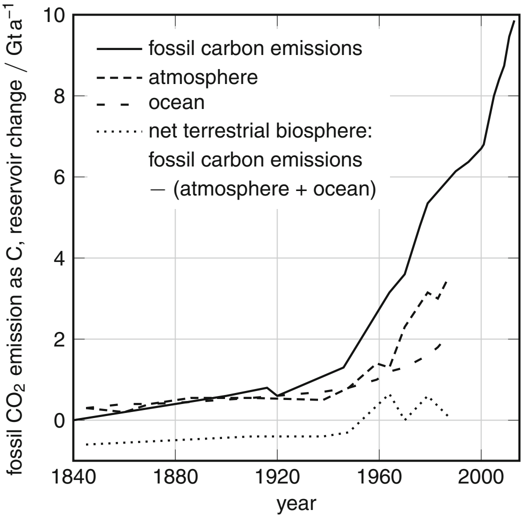


Fig. 5.5 History of total fossil CO_2 emissions (as carbon) and calculated global carbon reservoir change rates, *data sources* Schimel (2000), BP (2014), CDIAC (2014)

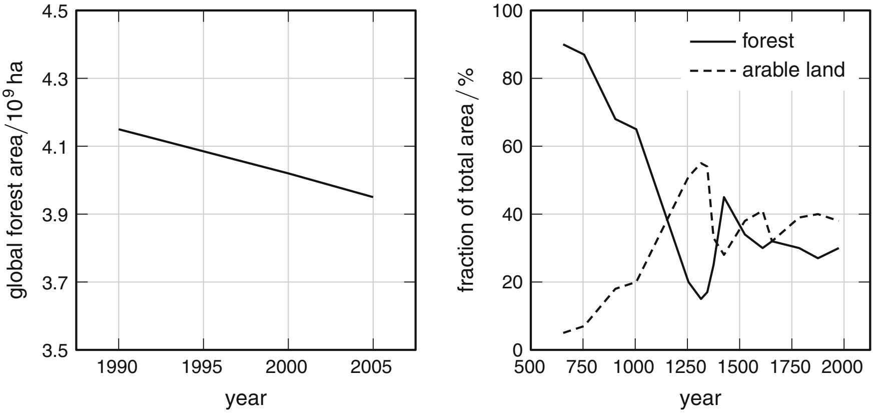


Fig. 5.6 Estimated changes of global forest area 1990–2005 and changing land use in Germany 655–1975, after: IPCC (2007b, p. 545) (*left*), Bork (1998), after Schönwiese (2008, p. 337) (*right*)

From a mass balance view, global CO_2 emissions (as carbon) lead to an increase of the atmospheric carbon reservoir equivalent to about 50 % of the total emission flow. The other half is distributed into other carbon reservoirs (ocean, biosphere). This can be seen in Fig. 5.5, where carbon reservoir change rates in the atmosphere and ocean represent estimates based on (concentration) measurement, whereas carbon reservoir change rate in biomass is given as a difference value as it cannot be measured directly. It is interesting to note that between 1995 and 2014 a considerable increase of total carbon emissions as CO_2 from combustion can be seen, in spite of the first political initiatives for greenhouse gas control mechanisms.

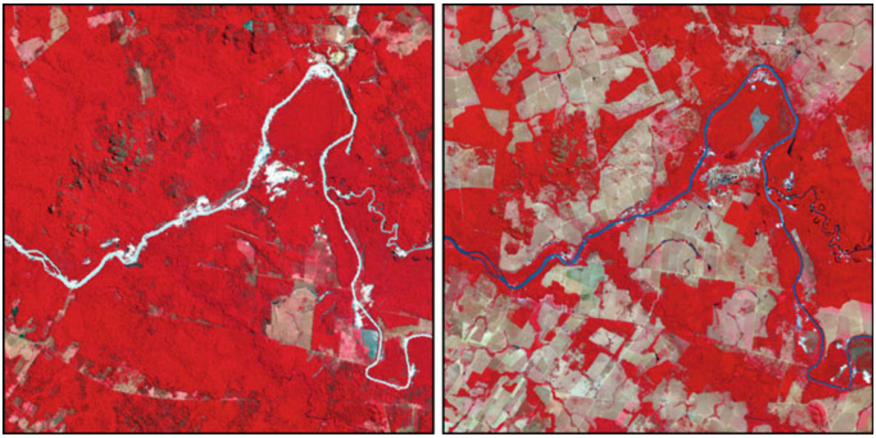


Fig. 5.7 Satellite images of the Mato Grosso region in central Brazil taken with NASA landsat 5 on August 6, 1992 (*left*) and with NASA Terra on July 28, 2006 (*right*), false-color images with *red* indicating vegetation, size of the depicted area approx. 400 km^2, images: http://earthobservatory.nasa.gov

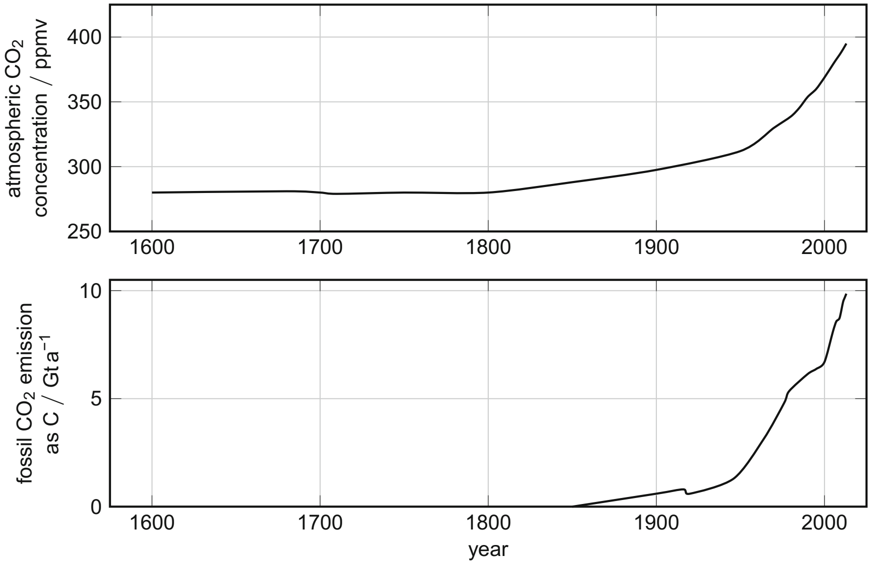


Fig. 5.8 History of atmospheric CO_2 concentration (*top*) and fossil CO_2 emissions (as carbon, *bottom*), trends and selected data, concentration data from ice core record and (since 1958) from Mauna Loa site, after: Schimel (2000), IPCC (2013, 2007a), Fischer Weltalmanach (2008)

Another anthropogenic effect on the global carbon system is changes in land use, which has always been part of the activities that shape the living environment of human communities. Global forest area has decreased between 1990 and 2005 at a rate of about 10×10^7 ha a^{-1} (Fig. 5.6, left) and at a slightly lower rate throughout the most recent years IPCC (2014), with carbon release into the atmosphere as a result. An example of intense land use change in a region in central Brazil between 1992 and 2006 is depicted in Fig. 5.7.

Fractions of forest area and arable land in Germany as an example country over the long time period between the year 650 until 2000 exhibit strong variations (Fig. 5.6, right). Changes in arable land reflect changing population figures and productivities, whereas changes in forest area are caused by the need for arable land and varying demand for wood (to be used for construction, energy source, etc.).

As a quantity that is easily able to be measured, CO_2 concentration gives a key information about changes in the global system. After a long period with CO_2 concentration levels below 300 ppm (hundreds of millennia), concentration levels have increased considerably since 250 years ago, in parallel with anthropogenic CO_2 emissions from fossil fuel application (Fig. 5.8).

5.2 Other Anthropogenic Material Flows

During the history of human societies flows of materials produced and processed by purpose have increased, especially in periods of early civilizations and since the beginning of industrialization. For very long time periods before the neolithicum,

Table 5.2 Characteristic mass flows of selected chemical elements on global scale, natural versus anthropogenic flows, *sources* see Figures in Chap. 4, Schlesinger (1997), Pinnekamp et al. (2013) (phosphorus) and estimates based on various sources

Element	$F_{m,\text{natural}}$ (t a^{-1})	$F_{m,\text{anthropogenic}}$ (t a^{-1})
O	295×10^9 Gross photosynthetic productivity	25.5×10^9 Fuel combustion
C	123×10^9 Gross photosynthetic productivity	7.8×10^9 Fuel combustion
N	155×10^6 Biological fixation	125×10^6 Fertilizer production
S	144×10^6 Sea salt droplets	110×10^6 Fuel combustion
P	186×10^6 Terrestrial biomass	29×10^6 Phosphate production
Fe	19×10^6 Continental dust	1650×10^6 Iron production
Zn	25×10^3 Continental dust	13×10^6 Zinc ore processing
Cl^-	6×10^9 Sea salt droplets	110×10^6 Salt utilization
Cl_2	0	65×10^6 Chlorine production

human life involved only those material flows required for biological functions: food as energy supply, air for breathing (and energy-supplying oxidation reactions), and water for supplying inorganic nutrients and electrolytes. Processing wood and other natural materials became important when tools were needed for hunting and farming or division of labor allowed individuals to develop capacities for making ornaments or jewelry. Later, humans developed simple technologies to convert metal oxide ores into metals by high-temperature processing (chemical reduction). The resulting new materials enabled human societies to produce more sophisticated tools and finally simple and then more complex machinery.

Mass flows of processed material were mentioned in the sections of Chap. 4 (Global Material Cycles). The numbers appearing in the global flow diagrams shown there are listed in Table 5.2, together with main natural flows for selected chemical elements. Among the main constituents of biological organisms, anthropogenic flows are lower than natural flows (e.g. fertilizer production versus biological fixation for nitrogen, fuel combustion vs. photosynthesis for carbon). For many metals, mass flows generated by humans largely exceed their natural flows. Here, human-induced changes in the movements through the atmosphere or natural reactions are relatively more significant. However, due to low vapor pressure and water solubility, long-distance environmental effects, in general, are only minor.

An interesting approach for making people in modern societies aware of the material flows caused by their lifestyle and consumer behavior was proposed in the 1990s (Schmidt-Bleek 1994). Material production for use in manufacturing consumer goods, fuels, etc. always means (co-)production of side or waste material flows. For example as an extreme case, when producing 2700 t of gold (which was the global production in 2011), a flow of rubble is generated during mining and processing on the order of 10^5–10^6 times larger (Fig. 5.9). This means that producing a golden ring leads to a flow of other materials on the order of 1000 kg. The most critical examples in terms of absolute quantities are the processing of iron, lignite, or tar sand, as large amounts of materials must be moved and/or processed.

Recycling materials after the use of consumer goods, machinery, etc. generally helps to decrease the flows of raw materials and fuels required for upgrading (see Sect. 5.4.3, Table 5.7, Fig. 5.19).

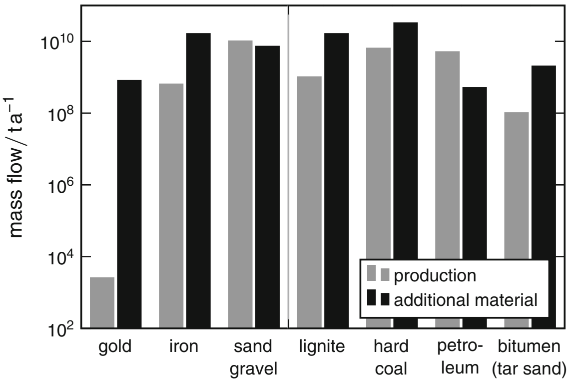


Fig. 5.9 Global mass flows of materials produced or used industrially and other materials connected with production, *gray bars* production, *black bars* additional material moved or treated during production, *sources* Fischer Weltalmanach (2008), Schmidt-Bleek (1994), own estimate (tar sand)

5.3 Global Utilization of Primary Energy

Since the beginning of industrialization, energy flows for human activities have increased significantly. Figure 5.10 shows historical trends of global energy flows due to human activities (with some uncertainty in the data available), present values

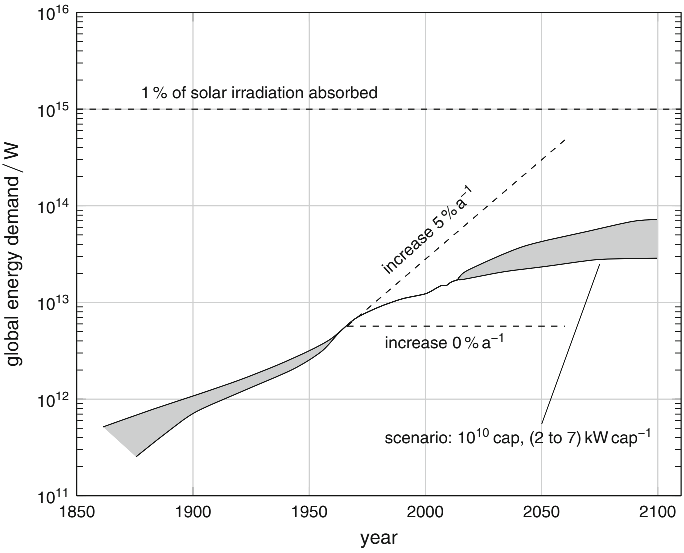
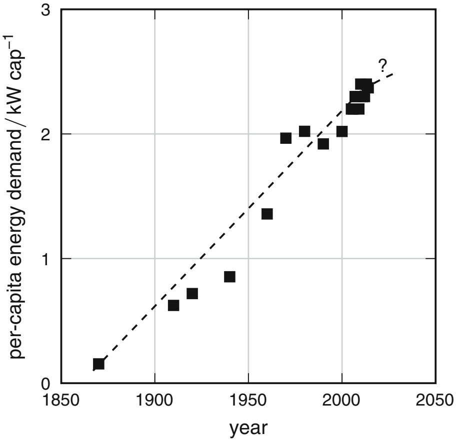


Fig. 5.10 History and future of anthropogenic energy flows on Earth, for explanation see text, *source* after Hagena (1995), BP (2014), Statista (2015)

Fig. 5.11 History of global average of per-capita energy flow, combining data from Figs. 2.13, 2.15 and 5.10, *dashed line* trend



(1.72×10^{13} W in 2014), and a range of future scenarios, assuming 10^{10} human beings on Earth and a specific primary energy flow of 2–7 kW cap^{-1}. The resulting flow in 2100 would be 7.2×10^{13} W, a fraction of about 0.1 % of the solar irradiation absorbed on Earth (see Chap. 3, Fig. 3.7). Also included are theoretical lines indicating growth rates of 0 and 5 % a^{-1}, both beginning with the year 1970. These theoretical lines are inspired by discussions in the 1970 s about the necessity of supplying energy with growth rates extrapolated from the years before. At that time, an absolute limit for human energy flows was seen to be at 1 % of the total solar irradiation absorbed. Climate change was not seen by the public nor by politicians as a criterion for seeing limits for energy conversion by humans on Earth.

Per-capita energy flow values for the global population, shown in Fig. 5.11, are generated by dividing absolute flows by the corresponding population values (see Sect. 2.2.5). Compared to the biological energy demand of human beings (about 0.1 kW cap^{-1}), these values represent a personal energy service introduced during the techno-economical process of industrialization.

The global mean values include significant variability from country to country and within a single country too, according to individual access to prosperity. Data for selected example countries at their present stages of economic development are plotted in Fig. 5.12 versus gross national income (GNI, as for 2006). There is a significant correlation between energy flow and GNI, although considerable scattering indicates that the correlation may be affected by external or internal factors (such as availability and cost of energy resources, climatic factors etc.). Gross national income presently serves as a characteristic quantity of national economies, and its variability for the range of national economies includes industrialized countries with lower growth rates and economies in development with present growth rates in a wide range between low and as high as 20 % a^{-1}.

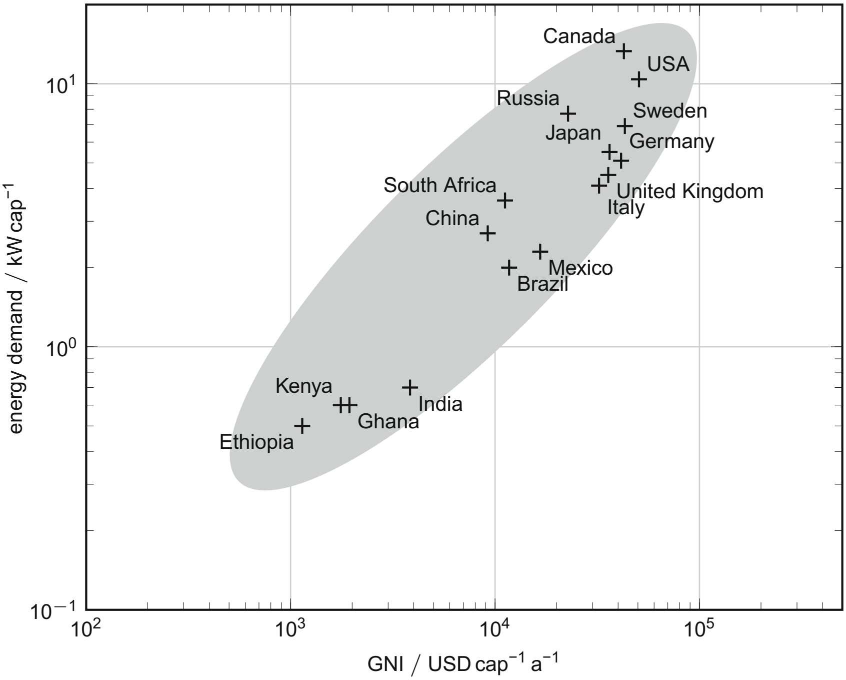


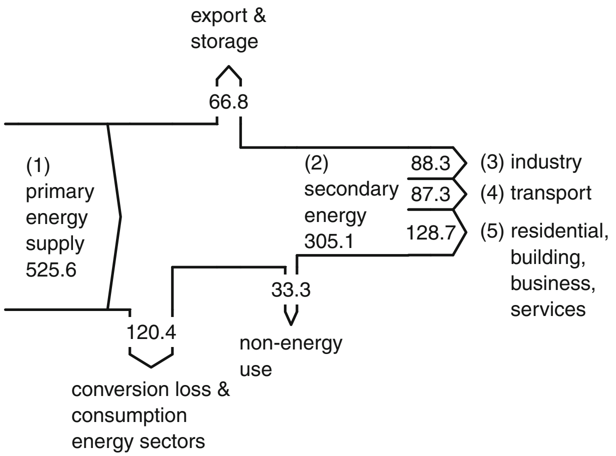
Fig. 5.12 Per-capita flow of primary energy and gross national income (GNI) in example countries (energy values: 2011, GNI: 2012), *data source* Statista (2015), GNI: Fischer Weltalmanach (2013)

5.4 Energy Flows in Germany

In the following sections, Germany is presented as an example of an industrialized country with respect to energy flows. These are commonly structured in different sectors, which help to identify areas of higher and lower values of energy demand.

5.4.1 Overview

Energy flows in a national economy are commonly structured as shown in Fig. 5.13. This representation gives a visual overview in quantitative terms, with the size of the arrows equivalent to quantities of individual energy flows. The gross structure includes primary energy inputs, their conversion into energy carriers (secondary or end energy) to be sold to consumers for application, i.e. to generate the form of energy desired in each of the following sectors: industry, transport, and residential/business/services. More detailed versions of Fig. 5.13 can be found for special situations in the openly accessible literature, e.g. in BWK (1999) for Germany in 1995. The analogous energy flow data for the global economy can be found in IPCC (2014, 2007b).



Distribution	(1)	Distribution	(2)	Distribution	(3)	(4)	(5)
Petroleum	33.7 %	Petroleum products	36.1 %	Mechanical energy	21.9 %	98.5 %	5.9 %
Natural gas	21.8 %	Natural gas	23.6 %	Heat low-T	9.7 %	0.5 %	72.4 %
Coal	25.0 %	Coal products	4.8 %	high-T	64.3 %	–	6.6 %
Nuclear	8.1 %	Renewables	6.6 %	Light	1.5 %	0.5 %	6.7 %
Renewables	10.3 %	Electricity	20.8 %	ICT[a]	1.3 %	0.4 %	4.4 %
		District heat	4.9 %				

[a] Information and Communication Technology

Fig. 5.13 Energy flows in Germany 2012 (Mt coal equivalent per year, coal equivalent: 29.3 MJ kg^{-1}), *data source* Energiebilanzen (2014)

Primary energy summarizes all energy inputs in their natural form (fossil and nuclear fuel raw materials, wind, hydro, solar, biomass, etc.). The distribution of these energy inputs as given below the flow diagram indicates that in Germany's energy supply system about 80 % of the total energy input presently comes from fossil resources. The combination of high fossil energy inputs and high energy demand per capita is not sustainable with respect to global development. Table 5.3 indicates that the distribution of primary energy inputs differ significantly from country to country. For example, availability of easy-to-mine coal leads to increased shares of coal (like in China). In contrast, rich natural resources or rural economies favor high contributions of renewable energy inputs (like in Sweden, Brazil, Kenya). The primary energy inputs to the global economy show that petroleum is presently still dominant, followed by coal, natural gas, renewables, and nuclear. The following trends can be seen in Table 5.3 for the (relatively short) time period from 2007 to 2012: (i) contribution of renewables is increasing except for countries with high industrial growth rates (China, India) or commitment to fossil resources (Russia), (ii) nuclear energy is increasing slightly in some countries, however decreasing on a global scale. The former can be attributed to the progress in renewable energy technologies and related political activities responding to climate change in various

Table 5.3 Distribution of primary energy sources in example countries (in %), values 2007 (italic) and 2012, *source* IEA (2009, 2014)

	Coal and peat		Petroleum[a]		Gas		Nuclear		Renewable[b]	
Brazil	*5.7*	5.4	*40.2*	41.5	*7.8*	9.7	*1.6*	1.5	*43.0*	42.0
Canada	*10.2*	7.3	*35.3*	32.6	*29.5*	33.2	*9.5*	9.8	*16.1*	16.8
China	*64.2*	68.0	*18.3*	16.0	*2.5*	4.2	*0.6*	0.9	*14.2*	10.9
France	*4.8*	4.5	*33.3*	29.1	*14.5*	15.1	*43.0*	43.9	*4.6*	7.3
Germany	*25.6*	25.0	*34.7*	33.7	*22.5*	21.8	*10.8*	8.1	*7.9*	10.3
Ghana	*0.0*	*0.0*	*31.7*	40.2	*0.0*	3.5	*0.0*	0.0	*68.4*	56.4
India	*39.4*	44.9	*24.1*	22.5	*5.5*	6.2	*0.9*	1.1	*30.1*	25.3
Kenya	*0.4*	1.0	*20.2*	16.7	*0.0*	0.0	*0.0*	0.0	*79.4*	82.3
Russia	*15.8*	17.6	*20.6*	22.3	*53.0*	51.2	*6.1*	6.2	*3.4*	2.7
Sweden	*5.2*	4.4	*28.5*	25.1	*1.7*	2.0	*34.0*	33.3	*29.0*	35.2
USA	*23.7*	19.9	*40.4*	36.0	*21.6*	27.8	*9.2*	9.8	*5.0*	6.5
World total	*26.0*	29.0	*34.3*	31.4	*20.5*	21.3	*6.2*	4.8	*12.9*	13.5

[a] Crude oil and oil products

[b] Hydro, solar, geothermal, biomass

countries, the latter is a consequence of growing skepticism towards nuclear energy, especially after the accident in Fukushima in 2011.

Conversion of primary energy inputs into secondary energy carriers includes a wide variety of technical processes. Prominent examples are power plants for electricity generation, petroleum refining for the production of liquid fuels for mobility, and the cleaning of natural gas according to specifications for distribution systems. Various examples with characteristic efficiency values are listed in Table 5.4. Energy loss in the conversion sector is significant, e.g. in thermal power plants without utilization of waste heat or in chemical upgrading of coal to clean liquid fuels (which is presently done in significant amounts only in South Africa and China).

Applying the secondary energy carriers such as fuels, electricity, district heat by conversion to the desired forms mechanical energy, light and heat (low- and high-temperature) again implies energy transport and conversion processes with limited efficiencies. For example, generating mechanical energy for moving an automobile by an internal combustion engine (Otto or Diesel) is done with an efficiency of 20–35 %, electric generation of light with 10 % efficiency or less (with higher values for today's new LED lamps). High flow densities of heat due to energy loss or heat dissipation in conversion and application may cause significant effects on local or regional climate. Examples are dense-population metropolitan areas (e.g. Manhattan) or areas with large power plant complexes.

Table 5.4 Characteristic efficiency values of selected energy/fuel conversion processes (from various sources)

	$\eta/\%$
Thermal power plants	
Coal-to-electricity	25–48
Coal-to-electricity with carbon capture + sequestration	<38
Coal-to-electricity + heat	70–85
Biomass-to-electricity + heat	70–85
Natural gas to electricity combined cycle	45–60
Fuel cell	
Gas/H_2-to-electricity	40–60
Fuel upgrading/conversion	
Petroleum refining	85–94
Tar sand upgrading	55–65
Coal-to-liquid hydrocarbons	30–45
Natural gas-to-liquid hydrocarbons	60–65
Biomass-to-methane	60–75[a]
	55–65[b]
Water electrolysis	
Electricity-to-H_2	ca. 80
Internal combustion engine	
Liquid fuel-to-mechanical energy	25–35
Gas/steam turbine	20–50

[a] Fermentation
[b] Thermochemical conversion

Box 5.2: Per-Capita Energy Flows in Germany

The energy flows used by individuals is of interest as a sort of personal energy intensity or personal energy footprint. Therefore, converting the energy flow values in Fig. 5.13 to W and dividing by the number of inhabitants (80.5×10^6 in 2012) leads to per-capita energy flow values in kW cap^{-1}.

Conversion factor

$$\text{Mt coal per year to kW: } \frac{29.3 \times 10^{12}}{365 \times 24 \times 3600} = 0.929 \times 10^6$$

Per-capita energy flow values in	kW cap^{-1}
Primary energy	5.4
Secondary energy	3.5
Industry	1.0
Transport	1.0
Residential + business + services	1.5

5.4.2 Energy Flows Related to Mobility and Transport

Individual transport today in Germany is dominated by automobiles. About 75 % of all personal distances are covered with automobiles, followed by metro/bus and other means (Table 5.5). As an average, each person in Germany travels a distance of 40 km per day, as determined by a public survey (Infas and DIW 2002). The respective value in 1950, i.e. before a period of high economic growth rates, was 4 km $\mathrm{cap}^{-1}\,\mathrm{d}^{-1}$. This individual mobility value is a kind of an indicator for economic prosperity. Changes in individual mobility behavior in Germany after 2002 were investigated in a study by Infas and DLR (2008). According to this study there have only been minor changes between 2002 and 2008. The historical development since the beginning of the 19th century is shown in Fig. 5.14 for France, which as a neighbor country of Germany, exhibited a similar economic growth history.

Specific energy demand of transport systems, expressed as energy per person-kilometer, varies considerably (Table 5.6). Technical improvements regarding energy efficiencies have contributed to a decrease in the past, whereas consumer behavior asking, for example, for larger-sized, safer (meaning heavier), and more comfortable cars has compensated a large part of the savings potential. Riding a bicycle is a very efficient way of moving whereas airplanes (as used predominantly for long distance) and automobiles exhibit the highest values. The example in Box 5.3 shows the energy demand according to Table 5.6, if a person has the choice between airplane, car, and rail to cover an annual distance of 20 000 km (equivalent to 55 km d^{-1}).

Table 5.5 Average daily mobility of individuals in Germany in 2002, rounded values, *data source* Infas and DIW (2002)

		Average daily distance km $\mathrm{cap}^{-1}\,\mathrm{d}^{-1}$	Average velocity km h^{-1}
Total		40[a]	30
	Automobile[b]	30	33
	Metro bus (short distance)	3	20
	Rail (long distance)	2	
	Airplane	1	
	Bicycle	1	
	Walking	1	
	Others	2	
Distribution	Leisure	31 %	
	Work and education	20 %	
	Shopping	19 %	
	Others	30 %	

[a] Value in 1950: 4 km $\mathrm{cap}^{-1}\,\mathrm{d}^{-1}$
[b] Passenger car only

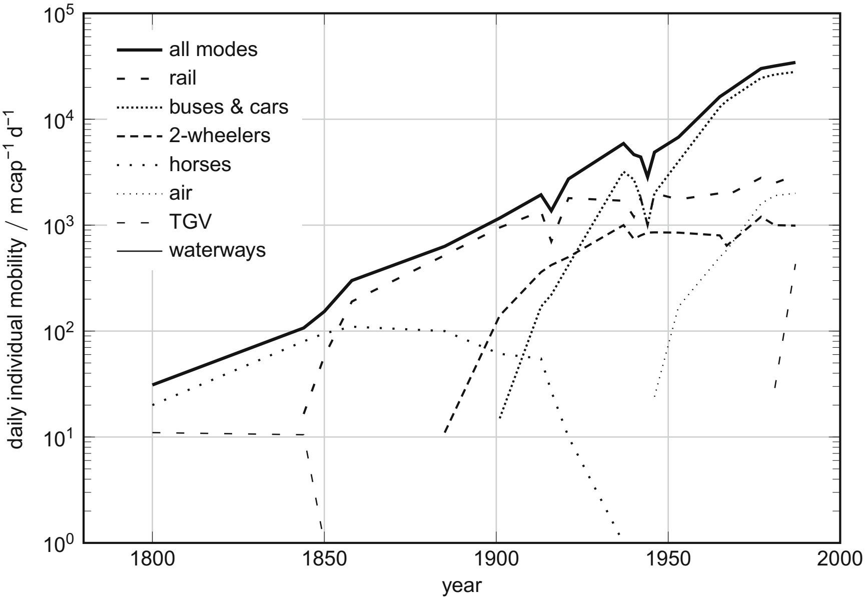


Fig. 5.14 History of average daily mobility in France 1800–1990, after: Grübler et al. (1993)

Table 5.6 Energy demand of different transport systems for individual mobility, *data source* IFEU (2012, 2006), modified and own estimates

	Energy source	Passengers per vehicle		Energy demand[a]	
			$\frac{\mathrm{L\,cap^{-1}}}{\mathrm{100\,km}}$	$\mathrm{MJ\,km^{-1}\,cap^{-1}}$	$\mathrm{kWh\,km^{-1}\,cap^{-1}}$
Airplane	Kerosene	200–600	2–5[b]	0.7–1.7	0.2–0.5
Automobile	Diesel[c]	4	1–3	0.3–1.0	0.1–0.3
	Hybrid[d]	4	0.8–2.4	0.25–0.8	0.08–0.25
	Electricity	4	–	0.2–0.5	0.05–0.15
Rail	Electricity	650	–	0.4	0.1
Bicycle	Food	1	–	0.06	0.02
Walking	Food	1	–	0.2	0.05

[a] All seats occupied
[b] Long distance (higher values for short to medium distance)
[c] Liquid hydrocarbons from petroleum (Diesel and gasoline)
[d] Liquid hydrocarbons and electricity conversion: energy content of hydrocarbons $43\,\mathrm{MJ\,kg^{-1}} \equiv 34\,\mathrm{MJ\,L^{-1}}$, $3.6\,\mathrm{MJ} \equiv 1\,\mathrm{kWh}$

The main reason for low efficiency values of automobiles is the internal combustion engine, that is used for generating mechanical energy from liquid fuels. Both Otto and Diesel engines exhibit efficiencies below 35 %, with slightly higher values for Diesel engines (Fig. 5.15). More than 95 % of all cars worldwide (presently about 1100 million) are fueled with gasoline or middle distillates produced via refining of petroleum with high efficiencies (up to 94 %, Table 5.4). If liquid fuels are produced from tar sand, coal, or natural gas via complex separation and chemical upgrading

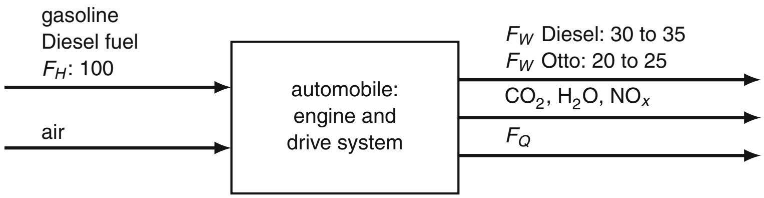


Fig. 5.15 Energy conversion efficiencies of internal combustion engine in automobiles, *numbers*: arbitrary energy units

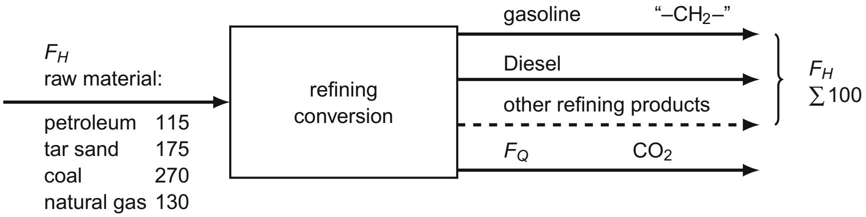


Fig. 5.16 Energy requirement for producing liquid hydrocarbon transport fuels (and other fuels and petrochemicals) from petroleum or synfuels via chemical conversion of alternative raw materials, *numbers*: arbitrary energy units, *source* Probstein and Hicks (1990), Schaub and Pabst (2011)

processes, then lower energy efficiencies of fuel production adds to the high energy demand of cars (Fig. 5.16). In the case of coal liquefaction, for example, overall energy demand is more than double as compared to the raw material petroleum.

Box 5.3: Case Study: Individual Energy Demand for Mobility

A person that has to travel for work purposes (for example, as salesperson for acquisition or marketing, R&D cooperation with partners etc.) has the choice to cover the assumed distance of 20 000 km a^{-1} either by automobile, airplane or railway. The personal energy flow needed is based on Table 5.6, assuming different levels of seat occupation. 1 year: 31.536×10^6 s

a) automobile: with 1.5 MJ cap^{-1} km^{-1} (seat occupation 33 %, in mid-size Diesel car)
   F secondary energy = 0.95 kW cap^{-1}
b) airplane: with 1.7 MJ cap^{-1} km^{-1} (seat occupation 75 %)
   F secondary energy = 1.13 kW cap^{-1}
c) railway: with 0.8 MJ cap^{-1} km^{-1} (seat occupation 50 %)
   F secondary energy = 0.51 kW cap^{-1}

In terms of secondary energy demand, railway among the transport systems has the lowest energy demand. For quantifying total energy demand, however, conversion efficiencies of primary energy conversion has to be considered (see Table 5.4).

5.4.3 Energy Flows Related to Industry

Developed economies today have various industrialized sectors for generating electrical energy and producing machinery, materials, and goods, each having characteristic networks of energy and material flows. Availability of cheap and sufficient energy and material sources has always been seen as a prerequisite for industrial and economic development. In the time of increasing energy prices, however, energy requirement is becoming a more critical criterion for strategic development of individual sectors. In the following, selected example sectors are discussed with emphasis on energy requirements.

In the electricity generation sector, obviously large energy flows are handled to generate the large contribution of electricity to total secondary energy (ca. 20 %, see Fig. 5.13). Most of the electricity in Germany has been produced in large- or medium-capacity thermal power plants until now. These power plants are based on steam or combined gas and steam cycles, with efficiencies limited according to the second law of thermodynamics (see Sect. 1.3.2). Figure 5.17 shows the resulting characteristic values, indicating that 40–80 % of the primary energy input is lost as waste heat. These large waste heat flows are generally dissipated to the local environment of the power plant (to river or sea water, ambient air) as the size of the flows is prohibitive for economic heat distribution and application. With respect to energy efficiency, natural gas-fired combined cycle processes are significantly better than steam cycle processes (50–60 % vs. 20–45 %). During the most recent years, there has been a strong increase

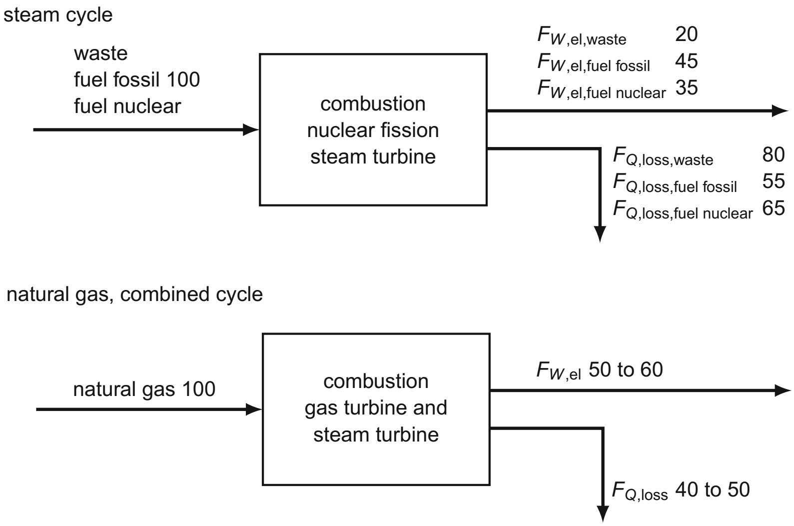


Fig. 5.17 Energy conversion efficiency in medium- to large-capacity thermal power plants (without utilization of waste heat), *numbers*: arbitrary energy units

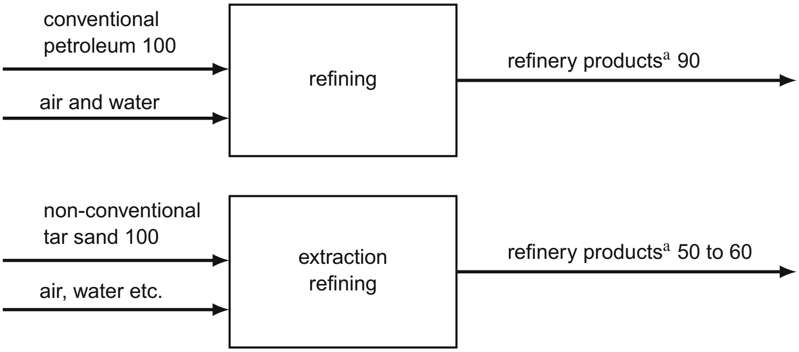
in wind- and solar-based electricity generation capacities, where electricity appears as primary energy, as well as a decrease in nuclear power generation (see Sect. 7.2.1).

The industrial sector producing heating or transport fuels according to environmental regulations and market demands has energy requirements strongly dependent on the kind of raw material. Natural gas can be cleaned in simple scrubbing processes with low energy inputs. Petroleum refining also requires only low energy inputs as the crude oil consists of nearly the same components that constitute the desired fuel product (hydrocarbons, liquid at ambient conditions). If tar sand serves as raw material, more effort (and energy) has to be spent to generate these components (as indicated in Fig. 5.18). With coal, this effect is even more pronounced.

The energy and material flows in all other industrial sectors are summarized in Fig. 5.19 in a simplified flow diagram. Highest amounts of energy are needed

a) in chemical conversion of materials involving endothermic chemical reactions at high temperatures (e.g. in iron ore reduction for steel making, electrolytic aluminium production from aluminium oxides, conversion of NaCl salt into commodity chemicals),
b) in high-temperature processing of metals and inorganic materials (cement, ceramics, glass), and
c) in manufacturing product goods whenever heavy materials have to be transported and moved (e.g. automated car manufacturing).

In cases where large energy inputs are required, there may be potential, after utilization, to save energy (and raw material resources) by reprocessing and recycling materials that can replace materials made from fresh resources. This is of particular interest, if large amounts of energy or materials can be saved. For a few selected materials, Table 5.7 gives specific energy demand values. In the case of steel as an



[a] main products: gasoline, Diesel fuel, heating fuel oils, liquid petroleum gas (LPG), petroleum coke

Fig. 5.18 Typical conversion efficiency of chemical energy in petroleum processing/refining, conventional (*top*), non-conventional feedstock tar sand (*bottom*), *numbers*: arbitrary energy units, own estimates based on Probstein and Hicks (1990)

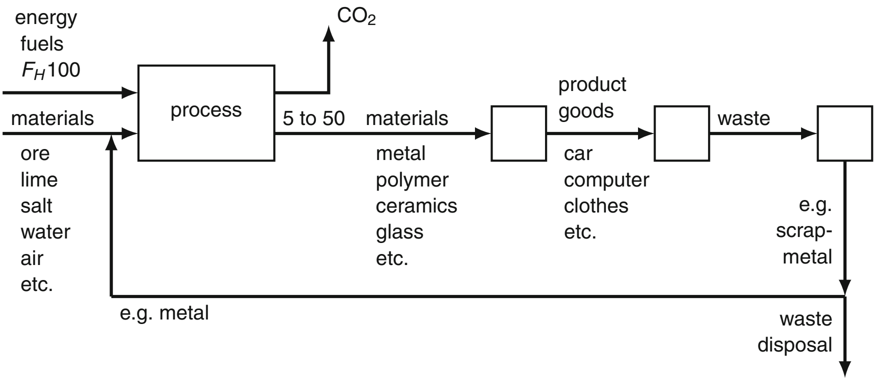


Fig. 5.19 Simplified scheme of energy and material flows in industrial material processing, product manufacture and utilization, *numbers*: arbitrary energy units, own estimates

Table 5.7 Specific energy demand for the production of different materials, *sources* Statistisches Bundesamt (2014), Fischer Weltalmanach (2008), Bossel (1994)

	Energy demand/MJ kg^{-1}		Production 2013
	Primary production	Recycling	$\text{kg cap}^{-1}\ \text{a}^{-1}$
Cement	4	n.a.	387
Glass	17	n.a.	93
Paper	9	5	140
Steel	25–50	20	441
Polymers	45–135	n.a.	212
Aluminium	200–230	5	14
Nitrogen fertilizer	44	n.a.	17

Energy content petroleum (oil equivalent): 41.87 MJ kg^{-1}

example, it is common practice today to recycle cars after final utilization in the form of scrap iron into the steelmaking process. The data listed in Table 5.7 allows for the calculation of an energy flow per-capita, related to the production of the individual material, either based on primary production or on recycling.

5.4.4 Energy Flows Related to Buildings and Domestic Use

Energy flows in buildings (residential, business, services) presently contributes about 42 % to the total secondary or end energy flow in Germany (see Fig. 5.13). The most significant part is used for low-temperature heat generation (72 %), followed by light, high-temperature heat, mechanical energy and energy for information and communication technologies (7, 7, 6 and 4 %). Heat is predominantly generated by

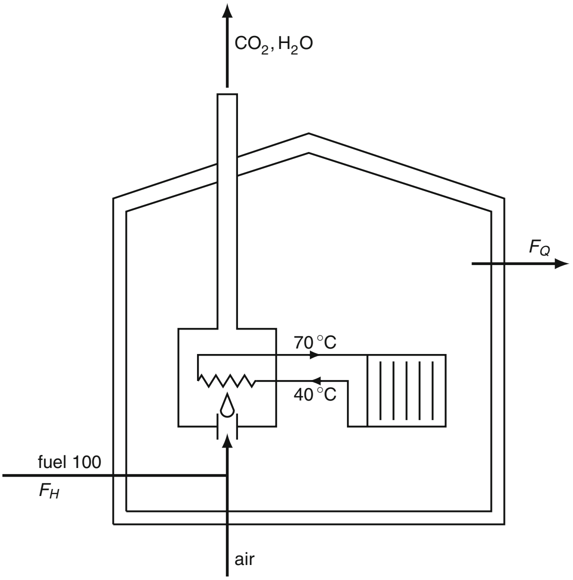


Fig. 5.20 Conventional (*central*) heating system of a residential building with heating fuel, example in Germany today, *numbers*: arbitrary energy units

fuel combustion (natural gas, light fuel oil). Mechanical energy for cooling devices and household machinery, as well as light energy are generated from electricity.

A conventional heating system in a residential building based on combustion of a gaseous or liquid heating fuel is shown schematically in Fig. 5.20. The fuel is burnt in a central combustion device/burner, with liquid water as a heat carrying medium to transport the heat generated to the individual rooms. If the flue gases from combustion are cooled in an efficient heat exchanger to temperatures low enough for condensation of product water (i.e. below about 70 °C), the heat of condensation can be recovered and thus heat loss with flue gases is minimized. Heat requirements for maintaining convenient room temperatures are primarily determined by climatic factors (outside air temperatures, wind) and secondly by the design and properties of the outer shell of the building (e.g. gain of radiation energy via windows or absorbing materials, minimization of heat losses by thermal insulation of the wall materials).

Standards for the design and construction of buildings regarding energy requirements for heating were established for the first time in Germany in 1977 (with thermal property specification of building materials and later maximum allowable energy input per residential area unit). Since 1977, driven by higher energy prices and political aims to decrease required energy flows and resulting CO_2 emissions, these standards have been set to lower limits several times (Table 5.8). Progress in creative architecture and in energy-oriented material development has allowed the combination of pleasant and healthy conditions indoor with low energy input flows.

Table 5.8 History of specific energy demand for heating of residential buildings, driven by limits defined in construction regulations (EnEV Energy Saving Regulation) since 1977, example one-family house in Germany

	Year of construction					
	1950–1977	1977–1982	1990	2002	2010	2016
$\frac{F_Q}{A}\Big/\mathrm{kWh\ m^{-2}\ a^{-1}}$	300–400	200–300	150–200	80	56	42
$\frac{F_Q}{N}\Big/\mathrm{kW\ cap^{-1}}$[a]			0.7–0.9	0.4	0.3	0.2

[a] With average area $A/N = 40\,\mathrm{m^2\,cap^{-1}}$

5.5 Correlation Between Energy Flows and Carbon Flows

In pre-industrial times, human societies were based on biomass, wind, and hydropower as energy sources. Larger amounts of coal and later petroleum and natural gas allowed for higher energy densities during combustion. Since the beginning of industrialization fossil energy sources have helped to significantly increase energy applications in human societies and developed into the major contribution to global energy supply (Table 5.9). The driving force for this change has been the accessibility of fossil resources and their economical utilization based on new technology developments. In recent times, renewable sources have been increasing, however fossil sources still contribute about 80 % to the total energy supply. Since 2005 there has been a strong increase in coal utilization in countries with fast growing economies. During the same time period, absolute generation figures from renewable resources have increased. However, the share of renewables has not increased due to the increase of total primary energy demand in the same time period.

During combustion (React. (5.1)), chemical energy is converted into thermal energy which possibly is converted afterwards into other forms of energy. The amount

Table 5.9 Distribution of world energy supply, historical development, values rounded, renewables by difference, *sources* WGBU (2003) until 1990, after (Jischa 2005, p. 76), IEA (2014)

	Fraction/%				
	Renewables[a]	Coal	Petroleum	Natural gas	Nuclear
1750	100	0	0	0	0
1850	64	36	0	0	0
1910	22	72	5	1	0
1930	17	60	14	5	0
1955	16	43	29	11	0
1965	10	37	37	15	0
1990	12	25	37	21	5
2006	14	26	34	21	6
2012	14	29	31	21	5

[a] Wood/biomass, hydro, wind, solar

of heat released can be quantified – based on chemical reaction enthalpies – by the higher heating value (*HHV*) and the lower heating value (*LHV*). The difference between *HHV* and *LHV* is the heat of condensation of the water formed. According to React. (5.1), energy conversion is linked to chemical reactions involving carbon.

$$CH_xO_y + \left(1 + \frac{x}{4} - \frac{y}{2}\right) O_2 \longrightarrow CO_2 + \frac{x}{2} H_2O \tag{5.1}$$

Chemical fuels are generally assessed according to various criteria: characteristic properties with respect to combustion, handling and storage, raw material availability, production cost, etc. Energy density, heating value, and specific CO_2 emission values are directly linked with the elemental composition regarding the main constituents carbon, hydrogen, and oxygen. Table 5.10 and Fig. 5.21 give an overview of hydrogen/carbon and oxygen/carbon ratios of important fuels (x and y values in React. (5.1)), both fossil and renewable. Also indicated is the range of coalification, i.e. the slow natural process over long time scales (order of million years). This process converts biomass into peat, lignite, and bituminous coal whenever in the Earth's history flooding with water or covering with ground material led to anaerobic conditions.

The higher heating value (*HHV*), according to the reaction enthalpy released during combustion (React. (5.1)), can be approximated by empirical correlations with the elemental composition (such as the examples given in Table 5.10). These correlations, though not suited for detailed engineering calculations, show the effects of stoichiometry on energy content and also on CO_2 emissions per *HHV* released when burning a fuel.

Whenever a chemical fuel is used as a secondary energy carrier, CO_2 emissions are not only significant during combustion, but also during the conversion process

Table 5.10 Molar ratio carbon/hydrogen/oxygen of chemical fuels, energy released during combustion (higher heating value *HHV*) and specific (fossil) CO_2 emissions, *source* Schaub and Pabst (2011)

	CH_xO_y [b]	*HHV* [c] MJ kg^{-1}	CO_2 fossil [d] kg GJ^{-1}
Natural gas	CH_4	55.7	49.4
Petroleum	$CH_{1.8}$	45.9	69.5
Bitumen [a]	$CH_{1.4}$	43.8	75.0
Bituminous coal	$CH_{0.8}O_{0.1}$	34.6	88.3
Lignite	$CH_{0.8}O_{0.3}$	26.3	95.0
Biomass	$CH_{1.6}O_{0.7}$	19.6	–
Wood	$CH_{1.37}O_{0.62}$	20.3	–

[a] From heavy oil, tar sand

[b] Weight fractions carbon in natural gas/petroleum/coal (dry organic matter), typical values: 75/90/75 %

[c] Per mass of dry organic fraction, calculated with correlation (Boie 1953; Meunier 1962) $HHV_{CH_xO_y} = (422.5 + 117.2x - 177.5y)/M_{CH_xO_y}$

[d] m_{CO_2}/HHV based on stoichiometry

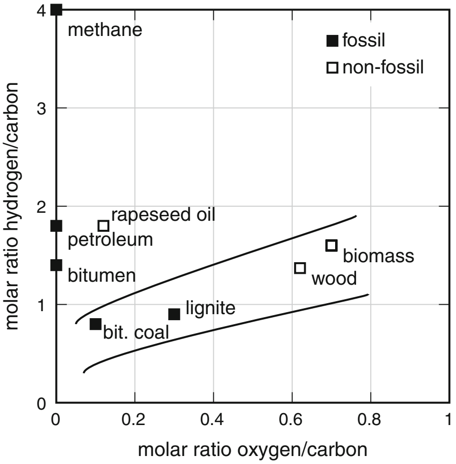


Fig. 5.21 Molar hydrogen- and oxygen-to-carbon ratios of chemical fuels and range of coalification (*range is between lines*)

of raw materials into usable fuels as energy carriers (e.g. oil refining, natural gas, or coal liquefaction, see examples in Table 5.4).

National economies and energy supply systems today depend on fossil energy sources to a different degree. The term CO_2 intensity is used for the correlation

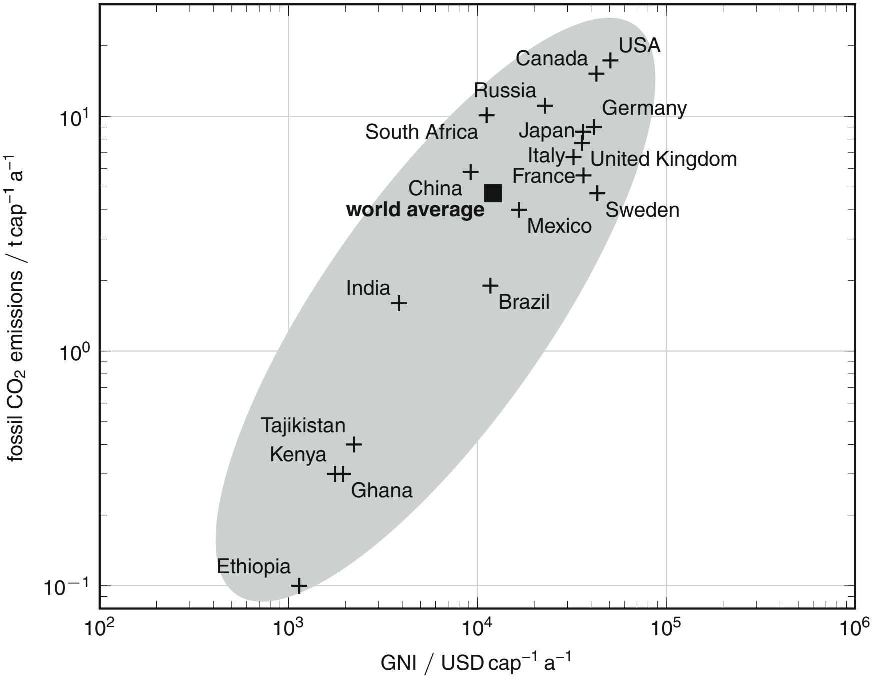


Fig. 5.22 Per-capita fossil CO_2 emission rate and gross national income (GNI) in example countries (values GNI: 2012, CO_2: 2009), *data source* Fischer Weltalmanach (2013)

between fossil carbon flow (with resulting CO_2 emissions) and gross national income (GNI). Figure 5.22 summarizes data for selected example countries, both industrial economies and economies in transition. Historical development has led to some correlation, which is characteristic of the low-cost availability of fossil energy source typical of the last 250-year-period. In absolute terms, Canada and the USA have the highest per-capita CO_2 emissions among the examples shown, followed by Western European countries and Japan. With respect to GNI values, CO_2 emissions are relatively high for example countries with high consumption of coal (e.g. South Africa, China, India), given the high specific CO_2 emission value of coal in Table 5.10. Among the example countries at the lower range of CO_2 intensity are Sweden and Brazil (with high contribution of renewables) and France (due to nuclear energy, as shown in Table 5.3). Figure 5.23 shows the global distribution of fossil CO_2 emissions, indicating that the Northern hemisphere makes the largest contribution to the increase of atmospheric CO_2 concentrations and global warming.

In conclusion, economic growth during the past three centuries was based primarily on the availability of relatively cheap fossil energy sources. As discussed in Chaps. 6 and 7, this correlation must and will be decreased, and thus changes in the structure of industrial economies and in consumer behavior will be required (transition of the energy system, see Sect. 7.6).

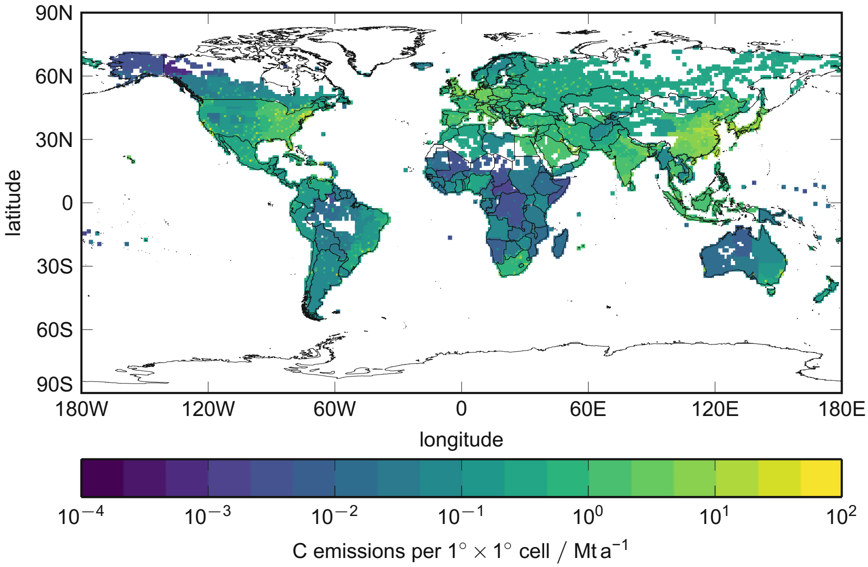


Fig. 5.23 Geographic distribution of CO_2 emissions (as carbon) originating from fossil fuel combustion, 1° spatial resolution (latitude/longitude), representation based on Andres et al. (1996), 2011 data from Boden et al. (2015)

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Chapter 6
Limits for Anthropogenic Material and Energy Flows

As human activities in recent (industrial) times cause large flows of materials and energy with significant impact on the environment, public discussion was stimulated in the 1970s and 1980s by publications about potential limits (e.g. by Meadows et al. 1972 or Barney 1981). The following discussion introduces five factors representing limits in different respects: availability of raw materials, productivity of photosynthesis, availability of renewable energy sources, stability of local and regional ecosystems, stability of climate system. Intriguing is the question, which of these factors might become most determining and when. Besides the five factors introduced, there are other aspects like availability of capital or political or military conflicts limiting human activities which are not included in this discussion here.

6.1 Reserves and Resources of Raw Materials

All finite, non-renewable raw materials found and used by humans on Earth – be it metal ores, inorganic salt, organic fossil, or nuclear energy carriers – are limited in their quantities. Besides the materials used as energy sources, there are more than 100 commercial mineral commodities that are mined, processed, and traded in the world market today (Barney 1981). Today many of these non-fuel materials, once the goods made from them are depreciated, are recycled (like iron, aluminium). In this way, the amounts of fresh or virgin raw materials are lower and resources can be saved (see Sect. 6.1.2). In contrast, in the case of fossil fuel materials, recycling is impossible because high-value (chemical) energy is converted to low-temperature heat at ambient conditions, equivalent to a loss in exergy. A common aspect of both non-fuel and fossil fuel raw materials are characteristic patterns in their production/consumption-time histories, to be seen in many examples in the history of human civilization. Petroleum will be discussed as a case study in the following, because it has exerted a very strong impact on global economies for more than a century.

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In discussing resources it is common to define two key terms – reserves and resources, and as variables the degree of geological assurance and economic feasibility (Barney 1981, p. 188). According to the definition commonly used, *reserves* include identified deposits known to be recoverable with current technology under present economic conditions. *Resources* include reserves as well as materials that have been identified, but cannot yet be extracted because of economic or technological limitations, and also economic or subeconomic materials, which have been estimated but not yet discovered. Compared to the reserves, the resources, therefore, entail far more hypothesis and much speculation.

6.1.1 Fossil Energy Sources

For petroleum, the history of world-wide discovery and consumption is shown in Fig. 6.1 (dominated by conventional, i.e. low-density crude oils, see below). The most significant discoveries were made after World War II, especially between 1955 and 1970, mainly in *giant* oil fields (Hiller and Kehrer 2000). Up until 1980, discoveries generally exceeded production/consumption rates. Since then – with increasing trend – production/consumption rates are higher than new discoveries, although there are still discoveries, according to ongoing exploration activities. In 1997, cumulative production/consumption was about 120 Gt, reserves 150 Gt, and resources 100 Gt, leading to a total *Estimated Ultimate Recovery* (EUR) of 370 Gt (according to Hiller and Kehrer 2000, as a relatively conservative value, see below). The values presented later for 2005 were 139, 159, 82 Gt, respectively, leading to 380 Gt EUR (Gerling 2005). The mass unit Gt stands for *oil equivalent*, a representative or standard quality with a lower heating value of 41.18 GJ t^{-1}.

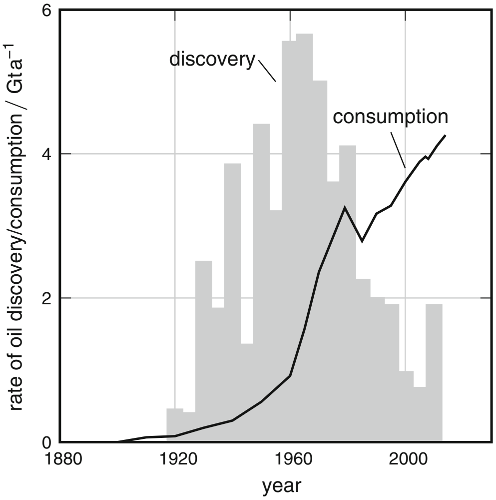
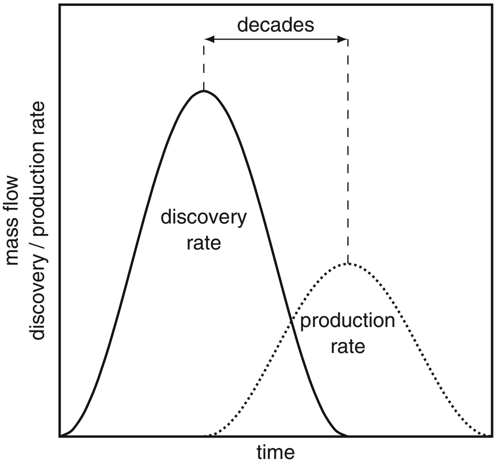


Fig. 6.1 Historical development of global oil field discovery (as 5-year average) and oil consumption rate, after Hiller and Kehrer (2000) (based on various sources), Miller and Sorrell (2014), MWV (2015)

Fig. 6.2 General pattern of resources discovery and production rates based on Hubbert (1969)



As for the patterns indicated in Fig. 6.1, during the 1950s Hubbert developed a generalized model. This was part of a significant effort to develop forecast methodologies for petroleum resources, given their enormous economic and strategic importance. Based on Hubbert (1969), production/consumption and discovery rates both exhibit Gaussian-type curves, with a time difference of their maxima in the order of decades (Fig. 6.2). The maximum or peak production/consumption and the depletion midpoint (when 50 % of the resources are depleted) coincide according to the model. When assessing the petroleum resources of the USA in the 1950s and their future perspectives, Hubbert predicted that oil production would peak in the late 1960s and thereafter domestic production and reserves would decline. He was not taken serious, at the time, but his estimate has proven accurate to a large extent.

Germany is an example country where petroleum production rates have already passed maximum values (peak oil). Therefore the curve shown in Fig. 6.3 can give an indication of what the global curve of oil production rates may look like Hiller and Kehrer (2000). There is currently very limited security of supply based on national oil resources in Germany today, when comparing consumption and domestic production rates of about 150 and 3.5 $\mathrm{Mt\,a^{-1}}$ (see Figs. 5.13 and 6.3).

As for the global situation, expected oil production curves strongly depend on the assumption made for the EUR (Fig. 6.4, based on Hiller and Kehrer 2000). Between the most conservative and the most speculative values indicated (250 and 800 Gt) the resulting curves are very different. Maximum production rates (*peak oil*) appear between 2005–2020 and 2050–2060, respectively. Very high figures of oil production projected for 2030 are published, for example, by the International Energy Agency and correspond to a demand increase by about 40 % compared to 2007 (IEA 2009).

Demand projections for petroleum may be intended to stimulate activities for exploration of new oil resources. In addition, oil exploration has always been intensified in periods of high oil prices. According to the definition of reserves (*recoverable under present economic conditions*) variations in oil price affect the quantity

Fig. 6.3 History of crude oil production in Germany and future trend, after Hiller and Kehrer (2000)

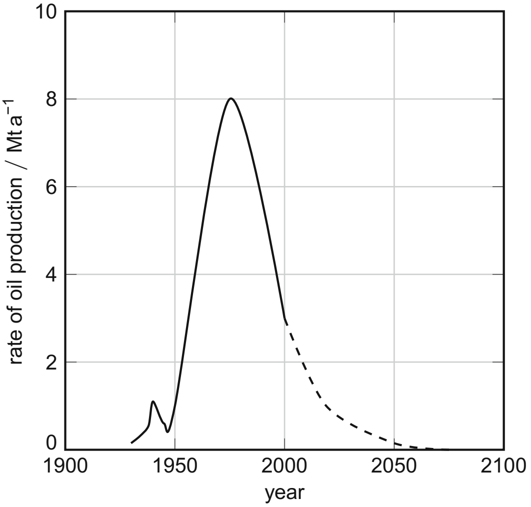
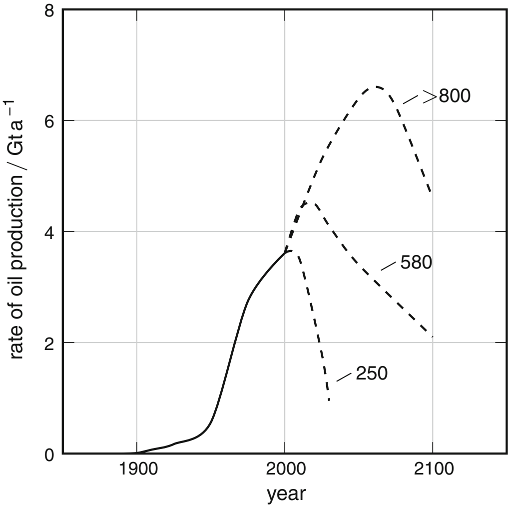


Fig. 6.4 Historical development of global crude oil production rate and future trends estimated on the basis of different assumptions for *estimated ultimate recovery* in Gt, after Hiller and Kehrer (2000)



of recoverable amounts. Figure 6.5 shows the schematic correlation where critical oil prices that allow for more expensive production methods depend on technical complexity and cost of production and processing methods. In any case, maintaining or extending the level of oil production will require large investments. Values in the range 200–400 billion USD can be found in the literature or in public statements (e.g. Sandrea 2004).

Actual reserves and resources for all fossil and nuclear energy sources are listed in Table 6.1 as published by the responsible German Federal Agency (BGR 2014). Due to the complexity of required definitions and data bases and also due to political

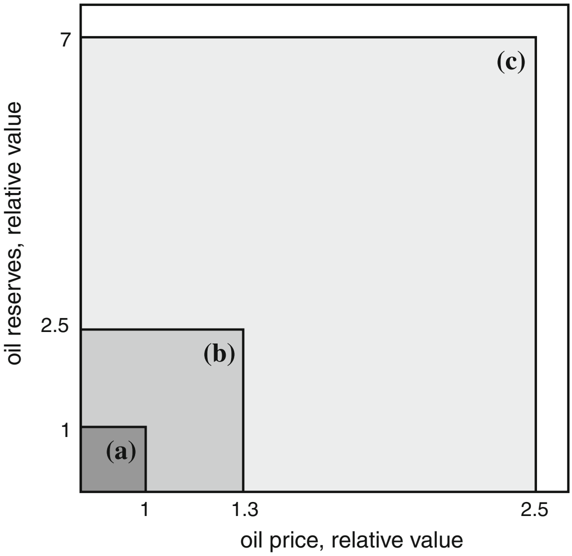


Fig. 6.5 Correlation of recoverable amounts of oil reserves and oil price (schematic, simplified after Hiller 1997), (*a*) conventional crude oil, including enhanced oil recovery (EOR), (*b*) oil sand, bitumen, (*c*) shale oil. From (*a*) to (*c*) increasing energy requirement during raw material production and processing: from (*a*) 10 % to (*b*) and (*c*) up to 50 % of *HHV* of feedstock (see Sect. 5.4.2)

interest, published figures may vary. The values are given as per end of 2013 in energy units, which allows the ability to directly compare the amounts of different energy sources. Non-conventional fuels are given separately and stand for heavy crude oils (density above 0.934 $\mathrm{g\,m^{-3}}$ or below 20° API), oil (tar) sand, shale oil, or shale and tight gas, coal-bed methane, and natural gas hydrates. The largest energy reserve (according to the definition above) in Table 6.1 is coal, followed by natural gas and oil. As for resources, there are very large amounts of coal and of non-conventional natural gas (and lesser oil).

In the case of petroleum and natural gas, significant amounts of non-conventional sources are trapped in underground sediments. Due to their low permeability, extraction requires combinations of drilling, hydraulic fracturing (*fracking*) and acidizing. The latter involves pumping acids into the well to dissolve caustic solids between the sediment grains of the reservoir rocks (WPC 2012). There is presently considerable public concern about the environmental risks caused by injecting liquid chemicals into the ground.

The sum of carbon stored in all fossil fuel sources comprises about 700 Gt (reserves) and 10 000 Gt (resources), based on the figures in Table 6.1 and carbon contents of 90 wt% in petroleum, 75 wt% in natural gas, and 75 wt% in coal. These values are included in the diagrams which show the global carbon cycle in Figs. 4.1 and 4.2 and must be viewed in comparison with the atmospheric carbon reservoir into which the fossil carbon is released upon combustion. Perturbation of the global carbon cycle will most likely become critical sooner than the depletion of fossil fuel resources.

The reserve values in Table 6.1 are used to estimate characteristic ratios of reserves and production/consumption for the fossil sources (with 2012 values given for

Table 6.1 Reserves and resources of non-renewable energy raw materials, as per 12/2013, definitions: see text, *data source* BGR (2014)

		Reserves EJ	Resources EJ
Petroleum	Conventional	7126[a,d]	6745
	Non-conventional	2011	11 462
Natural gas	Conventional	7318[b,e]	12 099
	Non-conventional	208	20 062
Coal		20 378[c,f]	489 766
Total fossil fuels		37 040	540 133
Total nuclear fuels		606	9858

[a] Equivalent to 170 Gt oil equivalent (OE)
[b] Equivalent to 193 000 Gm^3 (138 Gt)
[c] Equivalent to 695 Gt coal equivalent (CE)
Ratio reserves-to-production (BP 2014):
[d] 53 a
[e] 55 a
[f] 113 a

reserves and production). According to this definition, the characteristic times of *static availability* reflect a kind of global security of supply in each case. Values are between 53 years for oil and 113 years for coal.

Reserves and resources indicated in Table 6.1 are distributed among selected regions and countries throughout the globe. In particular, oil resources are rather concentrated in a few areas, conventional oil in the Middle East, Venezuela, Russia, Lybia, Nigeria, and Kasachstan, and non-conventional oil in Venezuela and Canada. Therefore security of supply of individual nations is also limited by political dependence and limited access to oil suppliers.

6.1.2 Other Important Materials

Besides carbon-containing fuel materials, many other raw materials contained in the Earth's crust are presently used by human societies in significant amounts. Their use generally involves physical and chemical processes of upgrading before consumer goods are produced (see Fig. 5.19). Here, recycling and reuse of the original materials or even of the goods after repair or renovation is possible with appropriate processing technologies and limited energy demand. This is in systematic contrast to the fossil energy materials. Combustion of coal, petroleum, or natural gas in order to generate heat or other forms of energy converts the fuel carbon to CO_2. Chemical recycling or reuse of the organic combustible carbon is not conceivable as a general principle according to thermodynamic criteria.

For each of the individual chemical elements used in industrialized economies, time-histories of production/consumption and discovery rates will follow, in principle, the general Hubbert patterns described for petroleum in the previous Section

(Fig. 6.2). Physical limitations are given by the estimated total available amounts of each element in the Earth's crust (Table 2.3). Global distribution of the concentration in deposits, their accessibility as well as the technological difficulty in processing determine the cost of the raw materials and the economic boundary conditions. In this sense, the limits for availability are not statically determined, but may change in the future.

An overview of selected elements that are used today is given in Table 6.2, with present consumption and recycling rates, estimated resources, and resulting estimates of static ranges (based on present consumption figures). Significant degrees of recycling are, for example, already achieved for the noble metals gold, silver, platinum, due to their high economic value, as well as for iron, whereas practically no recycling is practiced so far for phosphorous, although it is a base element for the global supply of food. As examples, lithium and copper as elements that are important for future renewable energy technologies (for storage and transport/distribution of electricity) and phosphorus are further discussed in the following.

Lithium

Lithium is the lightest solid element at normal temperature and a very reactive alkali metal. The Earth's crust contains lithium to an extent of about 60 ppm with the two main mineable sources being pegmatite minerals and continental brines, e.g. from dry lakes in South America (Wietelmann and Steinbild 2014). Technical uses of lithium comprise, among others, ceramics and glass, air conditioning, lightweight alloys, lubricants, and batteries. Lithium demand for batteries has risen steadily during recent years because rechargeable lithium-ion batteries are increasingly used in the growing markets of portable electronic devices and tools, grid storage applications, as well as hybrid and all-electric vehicles. If battery-driven vehicles become

Table 6.2 Overview of selected chemical elements of industrial importance, with respect to resource availability in the Earth's crust and present consumption, *data source* Sverdrup and Ragnarsdottir (2014) for recycling, U.S. Geological Survey (2015) for all other data, unless otherwise noted in text

	Reserves kt	Resources kt	Production kt a^{-1}	Ratio reserves-to-production a	Recycling %
Iron	87 000 000	>230 000 000	1 650 000	53	60
Copper	700 000	2 100 000	18 700	37	60
Nickel	81 000	>130 000	2400	34	60
Vanadium	15 000	>63 000	78	192	40
Lithium	13500	39 500	36	375	10
Cobalt	7200	25 000	112	64	40
Silver	530	n.a.	26.1	20	80
PGM[a]	66	>100	0.351[b]	188	65[b]
Gold	55	15	2.86	19	95
Phosphorus	8 000 000	>12 000 000	29 000	276	near 0

[a] Platinum Group Metals (Pt, Pd, Rh, Ru, Ir, Os) with approx. 90 % Pt, Pd
[b] Only Pt, Pd

the backbone of future individual mobility (cf. Sect. 7.2.3), the demand for lithium will rise dramatically. The world production of lithium amounted to 36 kt in 2014 with corresponding global reserves and resources estimated at 13.5 and 39.5 Mt, respectively (U.S. Geological Survey 2015).

The question of lithium availability is strongly linked to the number and type of batteries employed in future automobiles. Different options are under development ranging from smaller batteries in hybrid vehicles to very large units for all-electric cars. Speirs et al. (2014) calculated a theoretical lithium material intensity of 129.5 $\mathrm{g\,kWh^{-1}}$ for the conventional lithium-ion chemistry and estimated lithium intensities in technical batteries ranging from 190 to 380 $\mathrm{g\,kWh^{-1}}$. As an example, the annual production of 50 million all-electric vehicles with a battery energy content of 70 $\mathrm{k\,Wh^{-1}}$ results in a lithium demand of about 1 $\mathrm{Mt\,a^{-1}}$, while a fleet of 1000 million of these cars would contain some 20 Mt which is more lithium than the presently known reserves (Table 6.2). It is evident that this scenario of a strong market position for all-electric cars would require both a significant increase of lithium production and a considerable extent of recycling.

Copper

Copper, an element with a characteristic red color, is today the most frequently used heavy nonferrous metal and the third most important of all metals, after iron and aluminium. The upper part of the Earth's crust contains about 50 ppm Cu. At least 20 of the many copper minerals are important – typically sulfidic – ores which may reach concentrations of 50 000 ppm or more (Lossin 2012). Copper has several unique physical and chemical properties such as very high electrical and thermal conductivity, high ductility resulting in excellent workability, and remarkable corrosion resistance. Copper and copper alloys (e.g. with zinc or tin) are used in building and construction, electric and electronic products as well as many consumer products and industrial machinery. The world copper production reached 18.7 Mt in 2014 and the current global reserves and resources are estimated at 700 and 2100 Mt, respectively (U.S. Geological Survey 2015). Copper recycling has already reached a level of about 60 % (Sverdrup and Ragnarsdottir 2014) and will become even more important in the future because the static range of Cu reserves is less than 40 a (Table 6.2) while the present growth of copper products is relatively high (4.3 % expected for 2015, U.S. Geological Survey 2015). The future renewable electric energy supply (see Sect. 7.2.1) will require further large amounts of copper for wind and solar energy units as well as for stationary and mobile energy storage systems. However, it has been estimated that copper will be not a limiting component for a transition to renewable energies (Mocker et al. 2015).

Phosphorus

Phosphorus plays an important role as a component of nitrogen-phosphorus-potassium fertilizers for nutrient supply in cultivating agricultural crops and also in other industrial applications (for producing detergents or other chemical or nutritional compounds). Total consumption of P was $29\,\mathrm{Mt\,a^{-1}}$ in 2012, with more than 80 % contributing as fertilizer to the global supply of food and fodder (Killiches et al. 2013). For application as fertilizer, water-soluble phosphates are presently produced in increasing quantities exclusively from natural phosphate resources, i.e. without any considerable recycling of spent or excess phosphates. Therefore, supply shortage of phosphorus may arise as world population will further increase in the future, with expected potential increases of food and fodder demands as high as 70 % until 2050.

Nearly all the phosphorus in terrestrial ecosystems appears as calcium phosphate minerals, especially apatite (see Sect. 4.6). Mineable minerals are generally considered to have contents of P_2O_5 in the range 5–37 wt%. Besides phosphate and calcium, these minerals contain other chemical elements, such as fluorine, chlorine, thorium, uranium, vanadium, and cadmium, in varying amounts that affect their economic value. Cadmium and uranium may limit the application as fertilizer raw material. Raw phosphate minerals are treated using mechanical processes first (grinding, sieving, sedimentation) in order to produce a phosphate concentrate with 27–40 wt% of P_2O_5 ready for transport and further chemical processing with sulfuric acid and ammonia.

Published information on reserves and resources (as defined in Sect. 6.1.1) gives values that vary considerably. With present consumption figures, values of the static range of phosphorus reserves values can be calculated as high as 250–400 years (Killiches et al. 2013; Scholz and Wellmer 2013) or even higher than 1000 years (Kauwenbergh 2010). The process of exploration and reserves assessment on a global scale seems to still be ongoing. For example, a re-evaluation of reserves/resources occurred after 2009, leading to a very significant increase of global values. This makes recycling of spent or unused amounts of phosphorus and the development of innovative technologies economically less attractive in the short term, since supply and price of raw materials will probably remain stable for a considerable time.

6.2 Net Primary Production of Photosynthesis *NPP*

Biomass is presently the world's major source of food, stock fodder, and fibre and has the potential to contribute as a renewable resource of fuels, materials, and chemicals. Its availability is limited by two factors: (i) the rate of photosynthesis reactions, affected by photosynthetic species characteristics, soil quality, and climatic factors (photon flux density, temperature, water availability, etc.), as discussed in Sect. 3.4, and (ii) the availability of arable land or access to marine biomass, as determined by geographic factors and population density.

Each country in the world has within its borderlines a limited area suited for agriculture and forestry. As an example, Table 6.3 gives a list of selected European countries with their characteristic distribution of land use with potential for

Table 6.3 Agricultural areas and areas of interest for energy crops in selected European countries, after Holm Nielsen et al. (2007), based on FAO (2003)

	A_{total} 10^6 ha	$A_{\text{agricultural}}{}^{\text{a,d}}$ 10^6 ha	$\frac{N}{A_{\text{total}}}{}^{\text{b}}$ cap km^{-2}	$\frac{A_{\text{agricultural}}}{N}$ ha cap^{-1}	$A_{\text{arable land}}{}^{\text{d}}$ 10^6 ha
Bulgaria	11.1	5.2	66	0.69	3.3
France	55.2	29.3	121	0.50	18.5
Germany[c]	35.7	17.1	229	0.21	12.1
Ireland	7.0	4.6	65	1.04	1.1
Netherlands	4.2	2.4	404	0.09	1.3
Poland	31.3	15.2	123	0.45	11.4
Romania	23.8	14.5	89	0.67	9.3
Spain	50.5	27.9	92	0.79	12.7
EU 28	440	200	115	0.40	n.a.

[a] Incl. arable land, fallow/brackish, non-food, single/multi annual, permanent grassland
[b] Fischer Weltalmanach (2013)
[c] Land use distribution: agriculture and forestry 83 %, residential and roads 12.6 %, water (lakes etc.) 2.2 %, others 2.4 % (Fischer Weltalmanach 2004)
[d] FAO (2015)

energy crop cultivation. As expected, available agricultural areas per capita in individual countries differ significantly, depending mainly on population density. These examples represent industrial countries in moderate climate conditions, favorable for agriculture. The situation regarding sufficient biomass production is more difficult in other parts of the world with different biomes (see Table 3.3).

Yield potentials of energy crops are currently subject to significant research activities in many countries. Example results from a recent German investigation (Schaub and Vetter 2008) show varying yields for different locations in Germany, for each of several crops cultivated (e.g. miscanthus, grain, poplar). The energy crop yields can be compared quantitatively on a (dry) mass or a heating value basis, as shown in Fig. 6.6, with higher heating values *HHV* in the range 16–20 $\text{MJ}\,\text{kg}^{-1}$ dry biomass. According to these findings, dry biomass matter yields presently do not exceed 30 $\text{t}\,\text{ha}^{-1}\,\text{a}^{-1}$ (or 2 $\text{W}\,\text{m}^{-2}$). The lower part of Fig. 6.6 shows the resulting per-capita chemical energy generation in Germany, if a given fraction of the arable land is cultivated with energy crops. If, for example, 30 % of the actual agricultural area is used for energy crop cultivation with 30 $\text{t}\,\text{ha}^{-1}\,\text{a}^{-1}$ yield, a per-capita yield of 0.8 $\text{kW}\,\text{cap}^{-1}$ could be achieved. This represents about 15 % of the actual primary energy demand in Germany (5.4 $\text{kW}\,\text{cap}^{-1}$ in 2012, see Fig. 5.13 and Box 5.2). Higher contributions could of course be achieved after significantly improving energy efficiencies and thus decreasing primary energy demand (as indicated in Chap. 7). In addition, biomass can play a more important role as an energy source in countries with higher agricultural areas, e.g. in Eastern Europe (as shown in Table 6.3) and with higher biomass yields, e.g. in tropical climates (like, for example, in Vietnam).

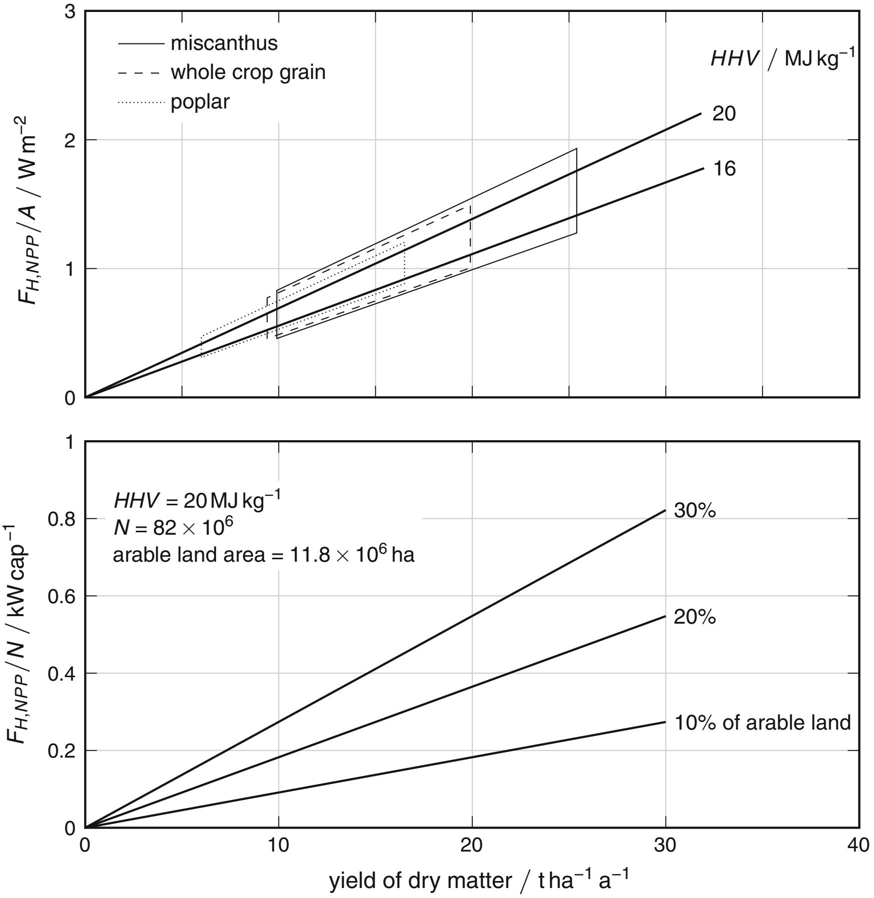


Fig. 6.6 Case study Germany: crop yields and chemical energy flow densities, ranges for energy crops (*top*), after Schaub and Vetter (2008), and potential contribution of bioenergy to primary energy supply (*bottom*)

6.3 Renewable Energy Sources

As the resources for renewable energy generation are limited, their potential has been assessed in numerous studies. A comprehensive survey of recent potential studies can be found in IPCC (2014). Definitions vary by study as do the data, as well as assumptions and methods used to estimate. Generally the physical and technical issues are discussed, with various kinds of constraints: practical, land use, environmental, and economic. As a general result of these studies it can be concluded that the potential for renewable energy generation is significantly higher than (even future) energy demands on a global scale, and in most cases on a regional scale.

Table 6.4 summarizes data from IPCC (2014) and a recent study by Jess (2012), the latter being based on a study by McKay (2008). These data indicate that the most abundant resource is solar radiation that can be used as source for various kinds of secondary energy (e.g. electricity, heat). All other renewable resources are significantly smaller. Based on these data, Jess calculated the potential availability of renewable energy in terms of energy per capita in a future world population situation of 9 billion inhabitants. The resulting value (around 9 $\text{kW}\,\text{cap}^{-1}$) is in the same range as the current primary energy demand of the richest industrialized countries (see Fig. 5.12).

6.4 Local and Regional Ecosystems

Industrialization led to negative consequences for local and regional environments. Emissions of gaseous, solid, and aqueous pollutants caused damage to air, water, and soil quality, which in turn did harm to living organisms, flora, fauna, and human beings. Effects were seen over distances limited by decay and removal mechanisms of the critical compounds emitted (see Sect. 1.1, Fig. 1.1). Significant bad experience was needed to gradually develop a conscience in human societies about the value of a clean environment (McNeill 2000). According to this experience, ensuring a clean and healthy environment can be seen as a limiting factor in the sense that the biological and psycho-social basis should be preserved in human societies. Three examples of local/regional environmental effects are discussed in the following.

Among the gaseous pollutants formed in industrial production processes and energy conversion in power plants, households, and automobiles, the most prominent examples are sulfur dioxide, nitrogen oxides, and unburnt organic species. In recent years, removal technologies have helped to clean off-gas flows emitted to the environment. The history of abatement of these pollutants in post-World-War II Germany can be seen as a successful example of improving the quality of the envi-

Table 6.4 Global technical potential of renewable energy sources, OE: oil equivalent = $41.87\,\text{MJ}\,\text{kg}^{-1}$

	EJ a^{-1}		$t_{\text{OE}}\,\text{cap}^{-1}\,\text{a}^{-1\text{c}}$	$\text{kW}\,\text{cap}^{-1\text{c}}$
	IPCC (2014)[a]	Jess (2012)[b]	Jess (2012)	
Solar (primary energy)	2000 to 40 000	2260	6.0	8.0
Wind (electricity)	100 to 600	188	0.5	0.7
Biomass (primary energy)	50 to 500	75	0.2	0.3
Geothermal (electricity, heat)	100 to 1000	64	0.17	0.2
Hydro (electricity)	30 to 50	49	0.13	0.2
Ocean (electricity)	7 to 300	8	0.02	0.03

[a] Extracted from various studies, IPCC (2014)

[b] Based on McKay (2008)

[c] Assumed future world population: 9×10^9

ronment by a combination of technology development and political commitment. Growing prosperity stemming from industrial development led to a situation where the society no longer accepted the negative consequences of a polluted environment, such as higher frequencies of sickness, increased mortality, bad conditions of trees in mountain forests, and loss of biodiversity in rivers and lakes.

As an example case, SO_2 emission abatement and resulting improvement of air quality in Germany between 1960 and 1995 are shown in Fig. 6.7. In the Ruhr district, a highly industrialized area in West Germany (with Gelsenkirchen as a representative city), air quality was very poor until the early 1970s, when coal-fired power plants and ferrous and non-ferrous metallurgical processes were gradually equipped with newly developed wet scrubbing processes. The political concept to gain a *blue sky again*, after a century of heavy industrialization, was created and was successful. A similar process occurred somewhat later in East Germany as shown for the cities of Leipzig and Chemnitz. These example data indicate that SO_2 emissions can be successfully controlled by means of gas cleaning processes.

As another example case, emission control of chlorine-containing organic molecules is highly developed today, after a critical incident at the herbicide production site at Seveso in Northern Italy in 1976 (see Sect. 4.7). During this incident, a failure in the reactor control system led to emissions of significant amounts of toxic dioxins causing significant damage to humans and animals (Heintz and Reinhardt 1993).

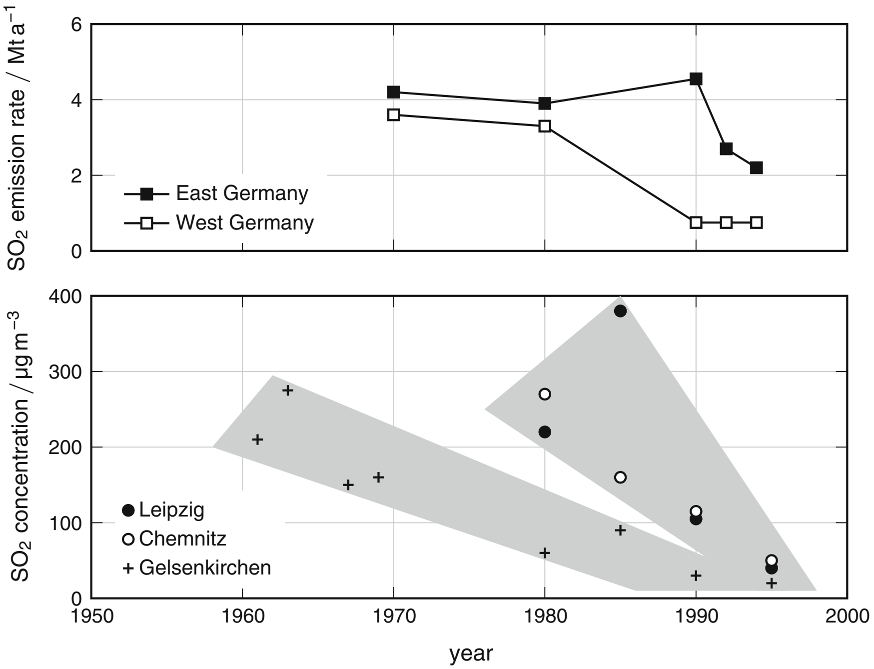


Fig. 6.7 Historical data of SO_2 emission rates (*top*) and SO_2 concentration in ambient air (*bottom*) in Germany, after Daten zur Umwelt (1997)

Since then, offgas cleaning technologies have been developed to very high standards for any plants where similar molecules could be formed, such as municipal or industrial waste incineration (applying adsorption or catalytic oxidation processes).

Protection of regional and local environments is also a criterion regarding the use of nuclear energy. If, during an accidental event, radioactive matter is released and deposited in the environment, accumulating in living organisms, this may lead to fatal consequences for humans and the surroundings they live in (as experienced during the Tchernobyl accident in 1986 (McNeill 2000) and the Fukushima accident in 2011). Since transport of radioactive material emitted to the atmosphere depends on the prevailing wind and precipitation situation, the distance range where detrimental effects are to be encountered may be very large (and even close to global). Although the risk of such incidents is considered to be very small, their severity may be extremely significant. In the case of the Fukushima accident, three out of six nuclear reactors in the plant melted down when the area was hit by a Tsunami, which was caused by an earthquake. Since then, radioactive materials have been leaking out of the plant for more than three years and the clean-up of the melted reactor cores is very difficult due to the high radioactivity.

6.5 Impact on Climate System

Historical climate data, such as the examples shown in Fig. 5.1, indicate that human societies since the beginning of industrialization 250 years ago have affected the global and regional climate system on Earth. Although this is a lingering process that is difficult to identify, to understand on scientific grounds, and to extrapolate in the future. It seems to be evident that its consequences will cause significant trouble for societies in different regions on Earth.

Human activities and cultures as developed in unique local and regional environments and ecosystems allover the Earth may be significantly disarranged if physical conditions of living change. According to observations and scientific progress in the recent past, societies have to reckon with the following (and other) negative effects (IPCC 2007a, p. 82): (i) Rise of global surface temperatures, with 13 of the 15 years between 2000 and 2014 ranking among the warmest years since 1850 (see Fig. 1.8). (ii) Distribution of precipitation and occurrence of heavy precipitation events have changed, with consequences for food production. (iii) The amount of ice on the Earth is decreasing and the rate of mass loss from glaciers is increasing. (iv) Rise of sea levels caused by thermal expansion of the ocean and loss of mass from glaciers and ice caps. As coastal areas are densely populated in many regions, this would seriously affect the living conditions of a large number of people.

Disturbance of natural material cycles and of the global energy system is seen as the primary cause of these anthropogenic effects. In particular, the shift of carbon into the relatively small reservoir of the atmosphere due to fossil carbon combustion is presently being considered. Based on the present knowledge of the interaction between the effects and the causes, the United Nations are negotiating on how to limit the negative effects of climate change.

The maximum allowable increase of global mean temperature is commonly used as criterion for limiting climate change, for which a value of 2 K compared to pre-industrial conditions is considered (Graßl et al. 2003, see Sect. 7.5). Herein it is rationale to avoid irreversible drastic changes in the climate system and to allow for realistic chances to take appropriate measures for adaptation. Measures for limiting temperature increase include reduction of CO_2 emissions and other greenhouse gases, and preservation of terrestrial ecosystems. An increase of 2 K corresponds to a CO_2 concentration in the atmosphere of about 450 ppm (calculated with present state-of-the-art models as CO_2 equivalent). According to the concept of radiative forcing RF, as introduced in Sect. 3.2, a temperature increase of 2 K can be expressed as a value for radiative forcing of $2.5\,\mathrm{W\,m^{-2}}$. This means that the effect is equivalent to an increase of net irradiation at the tropopause, i.e. at 15 km height, assuming radiative equilibrium.

Concentrations of 650 and 1000 ppm would lead to an increase of 3.6 and 5.5 K, respectively (IPCC 2007b, p. 826). The reference value is 280 ppm CO_2 at pre-industrial times. By keeping the mean temperature increase below 2 K, the following drastic changes can most likely be avoided (IPCC 2007c, p. 240): loss of large portions of endemic plants, bleaching or extinction of coral reefs, extinction of large portions of global biodiversity, severe coastal flooding each year, increase of water stress, decrease of food crops, etc.

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Chapter 7
Approaches to Global Development

This chapter discusses different aspects of future global development, as a consequence of the flow analyses presented earlier. Criteria for future development are presented, as well as technology and general policy strategies. The effect of individual life styles or living conditions on per-capita energy demand and emissions is demonstrated with some selected examples. Scenarios for future global CO_2 emissions and atmospheric carbon inventory are presented which are helpful in setting supranational agreements for future climate change policies. The transition process to a non-fossil energy supply system as recently initiated in Germany is outlined.

7.1 Criteria and Aims of Future Development

The concept of sustainability as mentioned in Chap. 1 addresses as an integrated approach economic, social and environmental aspects of global development. Within the context of this book, it leads to the following three most prominent consequences: (i) Material flows caused by human activities may induce detrimental, non-reversible effects on the global environment. Understanding of global material cycles with all relevant flows and reservoirs, is a prerequisite for taking adequate decisions for the future. (ii) Flows of fossil organic carbon connected with energy use of fossil chemical fuels (coal, petroleum, and natural gas) are most critical. They deplete resources of non-renewable and non-recyclable materials which are available only in limited quantity. And, they increase concentrations of carbon-containing gases in the atmosphere that affect the energy balance of the Earth. Therefore, criteria for dealing with anthropogenic carbon flows associated with energy conversion will be discussed in the following. (iii) Stability of the global carbon system requires the preservation of carbon reservoirs in the biosphere, in particular in tropical rain forests.

G. Schaub and T. Turek, *Energy Flows, Material Cycles and Global Development*, Environmental Science and Engineering,
DOI 10.1007/978-3-319-29495-7_7

Economy and Consumer Behavior

Given the easy accessibility and low cost of fossil energy resources in the past, national economies have developed with high (fossil) carbon intensities. Figure 7.1 correlates per-capita fossil carbon emissions with gross national income (GNI) in various countries, as introduced in Sect. 5.5 (Fig. 5.22). Example data and the marked range indicate a correlation for industrialized countries, economies in transition, and developing countries, as in an analogous plot with per-capita energy demand (Fig. 5.12). The dotted lines indicate directions suggested for future development: industrialized countries should significantly decrease their carbon intensity whereas developing countries should have a chance to take advantage of low-cost applications of fossil energy.

Industrialized economies should use their skills and economic potential to develop solutions that could be transferred to other countries and serve as models. Economies in fast transition should redirect their development in directions with low fossil carbon demands. Richer countries should create a culture where non-material values have higher priority among the variety of prosperity criteria (Table 7.1).

As a long-term direction for global development, assignment of fossil carbon emissions in terms of emission rights to each human individual may be a guideline (Graßl et al. 2003). This concept of *decrease and convergence* (of CO_2 emissions) may contribute to the break up of significant disparities in wealth and poverty that exist among and inside individual nations today. The idea of limiting and assigning individual carbon emission rights will be further discussed in Sect. 7.5.

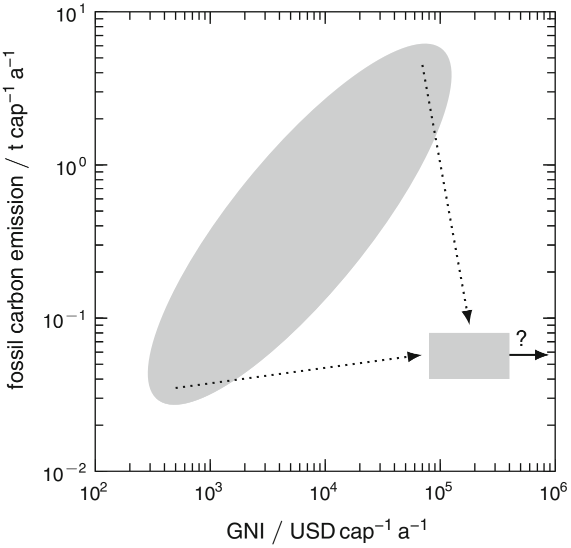


Fig. 7.1 Range of present per-capita fossil CO_2 emission rate (as carbon) and gross national income (GNI) in different countries (data see Fig. 5.22), *dotted lines* direction for future development

Table 7.1 Criteria for prosperity

Life expectancy Education Gross domestic product	Human development index (HDI)
Per capita	Housing area Number of vehicles Distance completed (mobility) ⋮ Cultural services

Technology Changes, Innovation

As a general guideline, human activities in energy conversion should make optimum use of natural cycles (Fig. 7.2). The continuous exchange of radiative energy between the Sun (resp. space) and the Earth should be used as much as possible by directly converting radiation into useful (secondary) forms of energy. In addition, the natural carbon cycle that uses a portion of solar radiation for photosynthetic growth of biomass, should be used (i) to generate food for the global population as practiced since long ago, (ii) to produce materials and goods made from biomass which are useful in daily life, and (iii) to generate useful (secondary) energy forms, with the particular advantages of chemical fuels (easy to store, high energy density). Biomass that is not used for any purpose decomposes slowly by oxidation in air, and its chemical energy content dissipates without being used.

If the strategies of making optimum use of natural cycles (i.e. of renewable energy sources) are successful, utilization of fossil resources can be minimized. In the subsequent Sect. 7.2, examples will be presented that are either already practiced today or are at a development stage, awaiting technical and/or economic breakthroughs. As an overview, Table 7.2 lists some measures to decrease anthropogenic fossil CO_2 emissions into the atmosphere.

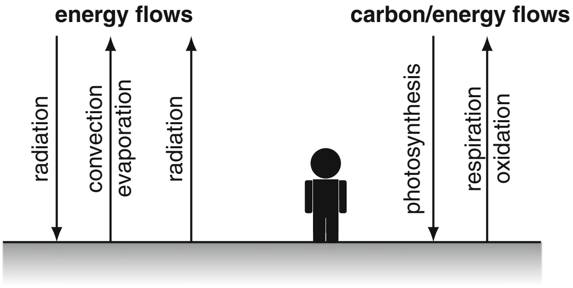


Fig. 7.2 Sketch of natural energy and carbon flows to/from the Earth's surface for integration of anthropogenic energy conversion and utilization (for details see Figs. 3.7 and 4.1)

Table 7.2 Technical strategies to decrease fossil anthropogenic CO_2 emissions from energy conversion and utilization for greenhouse gas control

Primary measures	Secondary measures
– Replace fossil fuels by (i) renewable fuels (biofuels), or (ii) non-chemical energy sources (solar, wind, hydro, ambient) – Increase energy efficiency of fossil fuel (and of upgrading processes) – Replace carbon-rich fossil fuels by hydrogen-rich fossil fuels	– Decarbonization: CO_2 sequestration, carbon capture and storage (CCS), before/after combustion

Land Use Change

A look at the global carbon cycle in Figs. 4.1 and 4.2 shows that not only is a decrease in fossil CO_2 emissions needed for CO_2 mitigation, but also for the conservation of the natural carbon reservoirs in vegetation and soil. In the past, changes in land use have lead to significant deforestation in order to ensure food production for growing populations or to provide wood for ship-building or for other uses in various parts of the world (see Figs. 5.6 and 5.7). With respect to a shift of carbon into the atmosphere, it is particularly the conversion of rain forest and bogland into farmland or meadows that is critical, as these areas exhibit the highest amounts of phytomass (see Sect. 3.4). Therefore, a definitive forest policy is as important as a definitive energy policy.

7.2 Examples of Sustainable Technologies

The actual energy flows in Germany, treated as an example country in Sect. 5.4, presently exhibit about an 80 % contribution of fossil primary energy sources and significant efficiency losses in the conversion and utilization sectors. The examples of technology alternatives in different energy sectors discussed in the following should therefore be directly compared to the energy flow diagram in Fig. 5.13. The discussion is based on various sources, among them the most recent IPCC reports (IPCC 2007a, 2011, 2014), which give a general overview of technology options for sustainable development.

7.2.1 Electrical Energy Generation

Sustainable technology options may be classified here into those that improve energy efficiency and those that reduce the use of fossil carbon-intensive fuels. In the case of energy efficiency, there have been incentives for continuous improvement since the times of increasing primary energy cost (e.g. crude oil prices from about 1 USD bbl^{-1} in 1960 to about 110 USD bbl^{-1} during the first half of 2014 and 30 USD bbl^{-1} at the end of 2015, with values as high as 150 USD bbl^{-1} during 2008, 1 bbl equivalent to 0.159 m^3). In addition, evolutionary developments based on the installed technologies generally require less investment.

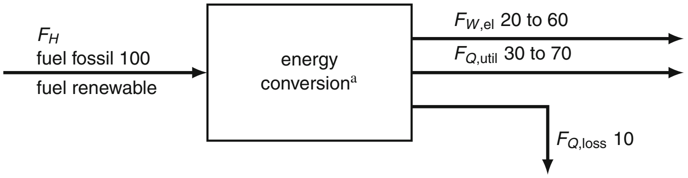
A list of today's conventional and potential future technologies for electricity generation is given in Table 7.3. Main incentives for changes in this area are (i) to avoid the large heat losses of central power plants and to use the heat for low-temperature heat supply in district heating systems, and (ii) to replace fossil (and nuclear) energy sources in the electricity generation sector with various kinds of renewable sources.

As an example of medium-capacity cogeneration power plants since the early 1980s, the city of Flensburg, Germany has used coal-fired boilers with a thermal input of 110 MW (Stadtwerke Flensburg 2010). A large fraction of the residential buildings (about 98 %) are connected to the district heat distribution grid. Overall energy efficiencies of about 80 % referred to as the thermal input can be achieved in this way (Fig. 7.3). Instead of coal or natural gas, biomass can be used as a renewable fuel, thus avoiding any fossil CO_2 emission from the combustion plant. Limitations in plant capacity exist in this case due to the lower energy density and therefore energy loss during biomass transport. In the case of smaller capacities – where economy of a steam turbine is not favorable – biomass can be gasified into a fuel gas which is then burnt in a gas engine (or micro(gas)turbine, fuel cell). A successful example is in operation in Güssing, Austria with an innovative fluidized bed gasification process and an 8 MW thermal input since 2002 (Repotec 2010).

Table 7.3 Technologies for electricity generation

Conventional	Future
– Large capacity thermal power generation, fossil, nuclear, steam and/or gas turbines – Water turbine – Storage: pumped storage hydro power	– Solar (thermal, photovoltaic)[a] – Wind turbine[a] – Fuel cell – Tidal water turbine – Small, medium, large capacity thermal power generation with cogeneration of heat, renewable raw materials (+ fossil, nuclear?) – Integration of small-capacity power generation in electric grids (virtual power plants) – Storage: pumped storage hydro power and various other technologies (e.g. electrochemical conversion to chemical energy carriers) – Carbon capture and storage (CCS) with larger-capacity fossil power plants (?)

[a] fluctuating/intermittent, integrated in distribution grids and combined with storage capacities (electrochemical, thermal, chemical, etc.)



[a] Alternatives: combustion and steam turbine
gasification and gas engine (or microturbine)
gasification and fuel cell

Fig. 7.3 Cogeneration of heat and electricity from chemical fuels, process alternatives for small to medium capacity combined heat and power (CHP) plant and yield estimates, *numbers* arbitrary energy units

Renewable energy sources (with the exception of large hydropower) are presently widely dispersed in comparison to fossil fuels. Energy densities are generally lower, therefore renewable energy must either be used in a distributed system or concentrated to meet the higher energy demands of cities or industries.

Hydroelectricity systems (water turbines) cover a wide range of capacity, from micro < 1 MW to small < 10 MW to large capacity > 10 MW (IPCC 2007b). Large capacity systems currently provide about 16 % of the global electricity, and more projects are under construction or consideration (although total capacities are limited world-wide, IPCC (2011)). There are hydroelectricity plants that are run as base load generators (such as the 12.6 GW Itaipu plant in Brazil/Paraguay) and others that are used mainly as fast-response peak load plants (e.g. as in pumped storage plants in Japan). Small and micro hydropower systems, usually run-of-river schemes, provide electricity to rural communities in both industrialized and developing countries.

Wind turbines are currently still small contributors to the global electricity supply, but are rapidly increasing in size and number. For example, new wind installation capacity has grown at an average of 28 % per year between 2000 and 2007 and at 20 % per year between 2010 and 2012, both onshore and offshore (IPCC 2007b, 2011). Offshore wind energy capacity will grow rapidly due to higher mean wind-speed conditions which offset the higher costs and thus leads to public acceptance. The average size of wind turbines has increased from less than 50 kW in the early 1980s to the largest commercially available in 2012 at around 7 MW, having a rotor diameter of over 120 m.

Solar electricity generation via thermal conversion can be done in manifold ways: (i) using parabolic mirrors or (ii) variable-position mirrors that concentrate irradiation on a receiver surface on top of a tower. In both cases, heat is transferred to a fluid medium that can drive a turbine to generate mechanical and finally electrical energy. Currently the most mature concentrating solar power (CSP) technology is solar troughs, with a maximum peak efficiency of 21 % in terms of conversion of direct solar radiation into grid electricity. Tower technology has been successfully demonstrated in the USA. The best location for CSP plants is at lower latitudes, where 1 % of the world's desert areas (240 000 km^2) could, in theory, be sufficient to meet global electricity demand as of 2030 (Philibert 2006; in IPCC 2007b). This would require a link to demand centres by high-voltage DC cables. This concept is part of the *Desertec* project recently suggested to connect the Mediterranean/North African region with Northern Europe and its high concentration of cities and industries (Desertec 2014).

Solar photovoltaic (PV) electricity generation is based on direct utilization of solar photons to create free electrons in special solid materials. Commercially available PV cells today are mostly based on crystalline silicon cells which achieve high efficiencies (up to 22 %, Photovoltaik 2016). Cost is a limiting factor, with cost reductions expected to continue with growing experience in mass production of solar panels and learning from project experience. Innovative cell materials like copper indium diselenide or organic polymers have prospects for further cost reduction. Recent examples of large-scale PV installations include Neuhardenberg (Germany, 145 MW), Cestas (France, 300 MW), and Solar Star (California, USA, 579 MW).

Decentralized electricity generation by solar PV is a feasible solution for villages with a long distance to a distribution grid, where providing light and television/radio is socially desired. Costs can be reduced if in new buildings PV systems are designed to be an integral part of the roof, walls, or windows. Combining solar PV power generation and heat utilization into one unit could make it more efficient if the heat produced from cooling the PV cells is used (Bakker et al. 2005; in IPCC 2007b).

There are other renewable energy sources and conversion technologies presently being developed for electricity generation, sometimes combined with heat: fuel cells with renewable fuels (e.g. biogas or fuel gas from biomass gasification or microalgae cultivation), geothermal, ocean (tidal) currents, wave power, ocean thermal, and saline gradients.

As a short-term mitigation strategy, carbon capture from fossil power plants and storage of CO_2 in isolation from the atmosphere are being developed in numerous R&D projects. Currently, large uncertainties relate to proving the technologies, anticipating environmental impacts and assessing the risks of losing significant parts of the carbon stored into the atmosphere.

Nuclear energy, presently about 7 % of total world-wide primary energy input, may also be seen as a way to make a contribution to carbon-free electricity and heat in the future. There is, however, controversial debate about the risks involved regarding operation and in particular nuclear waste treatment and management, proliferation, security, and long-term fuel resource constraints without recycling. After the incident in Fukushima in 2011, several countries (among them Germany) developed transition strategies to stop their nuclear programs and replace them with ambitious renewable energy programs (see Sect. 7.6).

As a conclusion, there is no single economic technical solution to reduce CO_2 emissions from the electrical energy sector. Depending on local/regional availability, there will be combinations of renewable energy technologies and fossil/nuclear technologies, the latter in transition to low carbon intensity or running out because of critical waste handling problems and safety aspects. Connecting many small scale electricity generators to the distribution grid with adequate control mecha-

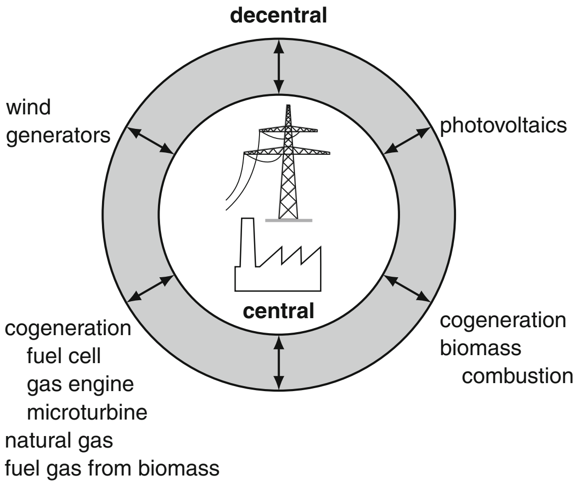


Fig. 7.4 Combination of central/decentral electric power generation with *virtual* power plants based on numerous small-scale power inputs into the electric grid

nisms (*intelligent* grids) is termed today as a *virtual* power plant (as combinations of small generators may replace individual large-scale power plants, Fig. 7.4).

7.2.2 *Heat Generation*

Technology options for heat generation must be classified according the characteristic temperature level of application: large amounts of low temperature heat are needed today for heating purposes whereas heat at high temperatures usually is required in the processing industries (metallurgy, cement and glass industries, etc.). In both cases, combustion processes are today most often used for heat generation (Table 7.4).

In the future, the aims should be (i) to minimize the demand for low-temperature heat, e.g. by improving thermal insulation of buildings, (ii) to supply low-temperature heat by using solar radiation or ambient thermal energy, thus replacing combustion as much as possible in this application, and (iii) to supply high-temperature heat as much as possible by burning biofuels instead of fossil fuels or by concentrating solar radiation. In some applications in the processing industries, fossil fuels may still be required (e.g. metallurgical coke in blast furnaces for iron ore reduction). In general, if fossil fuels are required, those which are poor in carbon and oxygen and rich in hydrogen should be preferred.

Active collector systems for capturing solar energy for direct heat are particularly suited for (i) small-scale domestic hot water installations for heating buildings or swimming pools, (ii) crop drying, (iii) industrial low-temperature processes, and (iv) solar-assisted district heating. Maximum achievable temperatures without concentrating the solar irradiation collected are limited according to the Stefan–Boltzmann law. This is shown for an example situation in Karlsruhe, Germany, at noon during a

Table 7.4 Technologies for heat generation

Conventional	Future
Low and high temperature	Low temperature
– Combustion of fossil fuels (gaseous, liquid, solid) in combustion chambers	– Solar gain in buildings combined with minimized heat loss (by thermal insulation)
	– Solar heat collectors
	– Biomass combustion
	– Heat pump
	High temperature
	– Combustion of non-fossil fuels
	– Heat generation from electricity
	– Concentration of solar radiation

sunny summer day (800 W m^{-2}) in Box 7.1, with a resulting maximum temperature of 71.5 °C. In current solar heat collectors, however, higher temperatures can occur, in cases with limited concentration by parabolic mirrors or with greenhouse effects due to glass shields.

Box 7.1: Maximum temperature of black body Exposed to Non-concentrated Solar Irradiation

The flow of energy that is emitted by a black body being at temperature T can be described with Planck's law of radiation, which, integrated over all wave lengths, yields the Stefan–Boltzmann law (Eqs. (3.1) and (3.3) in Sect. 3.1). As a consequence, maximum achievable temperatures, without concentrating the solar radiation collected by a solar collector, are limited. In an assumed steady-state situation thermal equilibrium prevails, with flux densities of incoming solar radiation equal to flux densities of outgoing black body radiation. A case study follows for a location in Germany (Karlsruhe, 49N, 8E) and summer mid-day irradiation (800 W m^{-2}). No convective or conductive heat loss is assumed, nor any greenhouse effect (Fig. 7.5). Equations (7.1) and (7.2) lead to a maximum achievable temperature of 71.5 °C, which confirms that solar heat collectors without concentration are suitable for low-temperature heat applications.

$$J_{\mathrm{solar}} = \sigma\, T^4 \tag{7.1}$$

$$T = \sqrt[4]{\frac{800\,\mathrm{W\,m^{-2}}}{5.67 \times 10^{-8}\mathrm{W\,m^{-2}\,K}}} = 344.65\,\mathrm{K} \tag{7.2}$$

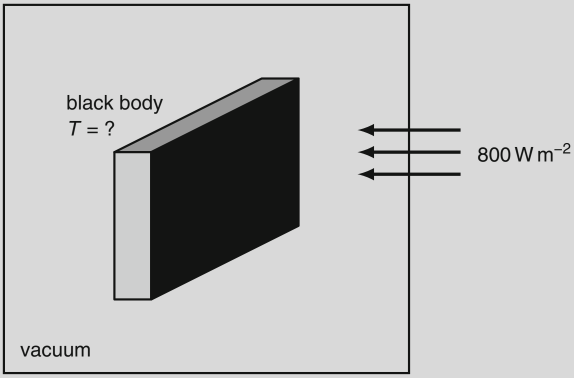


Fig. 7.5 Assumed situation to calculate temperature of black body exposed to solar radiation in Karlsruhe, Germany, on a summer day with 800 W m^{-2} irradiative flux density, according to Stefan–Boltzmann law

Maximizing solar gains and minimizing heat loss (through external building envelope or with air exchange) are primary elements of an integrated approach to building design (*passive house design*, Passiv 2015). Orientation and shape of buildings are optimized, and heating and cooling loads are minimized by providing high-performance envelopes (Fig. 7.6 and Table 7.5). Specific energy demands can be reduced to below 15 kWh m^{-2} a^{-1}, significantly lower than present and past building

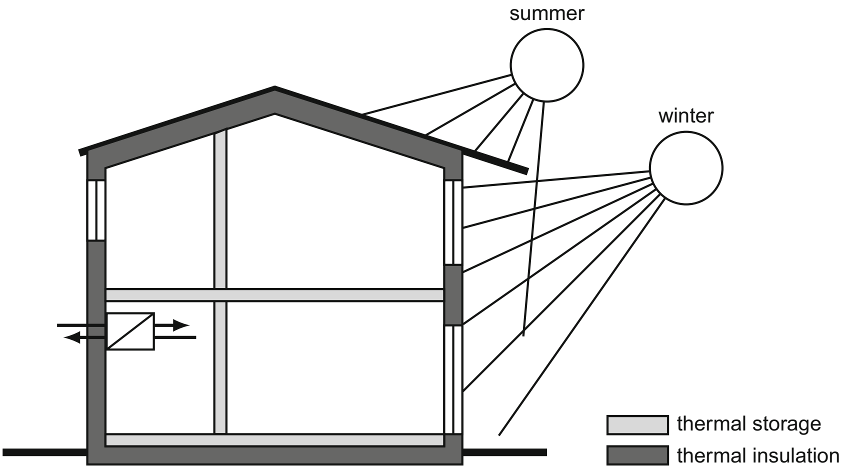


Fig. 7.6 Concept of passive solar energy building, with efficient thermal insulation, high solar energy gain, heat storage during winter time, heat recovery by air exchange

Table 7.5 Measures for thermal energy optimization of buildings

Aim	Measures
Maximization/control of solar gain	– Direction of exposure to solar radiation – Design of building surface (glass areas, convective heat transfer for cooling)
Minimization/adjustment of heat loss	– Thermal insulation (roof, walls) – Heat exchange between air inlet/outlet
Heat storage	– Day–night – Warm–cold season
External supply of heat (minimized)	– Environmental heat via heat pump – Combustion of fuels – Solar collectors etc.

designs (see Table 5.8). In addition, minimizing heat loss has proven to be comfortable for the users: warm inner surfaces, in particular warm inner window surfaces, and no drafts near the external walls.

Given the significant performance improvement of passive buildings, it can be foreseen that future building designs will be generally made based on the following principles: (i) low heat transfer values of external walls and windows (around 0.1–0.15 and 0.8 $\mathrm{W\,m^{-2}\,K^{-1}}$), (ii) passive solar gains of about one third of the remaining heat loss in winter, (iii) heat in exiting air recovered during ventilation with minimum 75 % efficiency, and (iv) low additional heat requirements during winter time supplied by low-temperature heat (solar, ambient) or a small-capacity furnace.

The integrated design process involves all major parties, from building users to architects to equipment suppliers. If made properly, the significant energy savings can be achieved at little or no additional investment cost (as an order of magnitude: passive house design standard in new building about 10 %, in old building renovation about 15 % additional cost as compared to conventional standard).

In existing older buildings with low thermal performance, improvements can be achieved when thermal insulation is added to external walls, old windows are replaced and other sources of heat loss are identified and avoided (Energieberatung 2015). Low-heat conductivity materials (foamed polystyrene, stone wool, etc.) are now widely used with success. In the case of polystyrene, the energy needed to produce the required amounts from petroleum is almost equivalent to the savings in energy for heating during one winter (Box 7.2, example one-family house in Karlsruhe, Germany). There is still some controversy about the technical details of insulating existing buildings (e.g. regarding optimum materials or how to avoid organic matter growing on external surfaces). However, experience is increasing with wider application and will ultimately lead to wide-spread know-how in the future.

Box 7.2: Thermal Insulation of Residential Building

Heat loss during winter and overheating in summer time can be significantly decreased if the envelope of a building is covered by a layer of thermal insulation material. Either foamed polymers or inorganic materials can be used, applied in a fixed layer with 10 to 20 cm thickness. In Germany, this is currently a significant activity, because energy demand for supplying low-temperature heat gives a high contribution to secondary energy demand (Fig. 5.13).

The case of a one-family house in Karlsruhe, Germany is presented, where thermal insulation was added to an existing building as a foamed polymer layer (polystyrene). The comparison of petroleum consumption for the production of the insulation material (as estimated) and energy savings due to lower heat loss during winter time (measured in the example house) is of particular interest. The input data for the simple calculation and results are listed in Table 7.6.

The resulting saving of fuel oil amounts to about 28 800 MJ a^{-1} for the 135 m^2 house. This is equivalent to about 40 % of the heat requirement before the addition of the thermal insulation layer. Compared to this saving of fuel oil per year, the amount of petroleum needed to produce the polymer material for insulation is estimated as 30 240 MJ, which is about the same amount of energy as it is saved by the insulation in one year.

Table 7.6 Thermal insulation of an example residential building, comparison of energy requirement for the production of insulation material (polystyrene from petroleum) and energy saving (fuel oil extra light, details: see text)

Data of building			Production of polystyrene	
Living area	135	m^2	$m_{\text{petroleum}}$	$1.4 \times m_{\text{polystyrene}}$
Surface area insulation	180	m^2	Energy content	30 240 MJ
Insulation thickness	0.14	m	(based on $HHV = 42\,\text{MJ}\,\text{kg}^{-1}$)	
Volume of insulation material	25.2	m^3		
Mass of insulation material (with $\rho = 20\,\text{kg}\,\text{m}^{-3}$)	504	kg		
Resulting saving of fuel oil	28 800 MJ a^{-1}			

7.2.3 *Energy Supply for Mobility and Transport*

Transport of goods and individual mobility are increasing around the world as less-developed economies grow, analogous with historical trends in industrialized countries (see the example France in Fig. 5.14). Today, transport predominantly relies on petroleum (about 94 %), a fossil liquid fuel with high energy density that is easy to refine and to handle. Land-based transport had a share of 78 % of total end energy use for transport worldwide in the year 2000 (with air- and water-based transport 12 and 10 %, IPCC 2007c, 2014). Therefore, in the following, the discussion is concentrated on land-based transport.

Worldwide numbers of vehicles range between less than 10 to about 750 per 1000 persons in different countries (World Bank 2015), with highest values in North America which, based on geographic factors together with early innovations in petroleum refining and car manufacture technology, were the first to create an automobile culture during the last century. Assuming an average car density of 500 vehicles per 1000 persons for a future world population of 8.5 billions would mean a total of more than 4 billion cars (as compared to about one billion in 2013).

Obviously, changes in technology and in consumer behavior must be significant in order to secure basic mobility demands and to decrease specific energy and material flows related to the transport sector. Future technologies and changes in individual mobility behavior include different options which are briefly described in the following, most of them related to private cars.

General Technology Development

In order to improve fuel economy, future automobiles should have as key features (i) vehicle mass and engine power reduced by new designs, smaller size, and new materials, (ii) rolling resistance and reduced drag coefficient, and (iii) increased engine efficiency. In the European Union, there is a target of 90 $\mathrm{g\,km^{-1}}$ fossil CO_2 as the average emissions from new cars for 2020, as compared to about 140 $\mathrm{g\,km^{-1}}$ in 2010 (IPCC 2014). A combination of general technology development, introduction of electric drive systems for short distance, and biofuels is supposed to meet this target. Lowest values, achieved in small-size cars manufactured commercially, today are about 90 $\mathrm{g\,km^{-1}}$ (equivalent to 3 L fuel/100 km).

Hybrid Vehicles

Combinations of a combustion engine with an electric motor offer the possibility to recover and store braking energy. This leads to an improved overall efficiency of the car. Critical aspects include higher complexity and investment, given the two sources of propulsion.

All-Electric Vehicles

The all-electric cars currently being developed are driven by electric motors with high efficiencies (usually above 90 %). However, the overall efficiencies include electric power generation, which in the case of fossil primary energy may lead to significant

CO_2 emissions (see Sects. 5.4.3 and 7.2.1). Depending on a specific electric power generation mix (coal/nuclear/renewables/natural gas), resulting fossil CO_2 emissions may be higher than from efficient combustion engine vehicles, fueled with petroleum-derived fuels. Most critical for electric vehicles is the need for a reliable, low-weight, and low-cost energy-storage component. Here, various systems are being developed for automotive applications, starting from current Li ion batteries with a typical energy density of 0.5 $\mathrm{MJ\,kg^{-1}}$ (as compared to 40 $\mathrm{MJ\,kg^{-1}}$ for hydrocarbon gasoline) over lithium sulfur to metal air batteries.

Biofuels

As photosynthesis productivity (*NPP*) is limited in the cultivation of biomass for food, feed, and fuel (as discussed in Sects. 3.4 and 7.2.4), biofuels can contribute only to a limited extent. In combination with other options (general efficiency increase, renewable electricity-driven vehicles, changes in consumer behavior, etc.), however, biofuels can be a significant contribution in some regions, sustaining regional agricultural structures (see Sect. 7.2.4). Potential negative side-effects (e.g. carbon release due to changes in land use) can be identified by a life cycle analysis, a systematic method for the assessment of environmental impacts of transport technologies.

Non-motorized Transport

A considerable number of trips made in cars at present cover distances of less than 5 km. Therefore, there is a significant potential for the reduction in CO_2 emissions by switching from motorized to non-motorized or hybrid transport, i.e. to cycling or e-cycling and walking. In many cities, local authorities seek to enhance cycling by providing better cycling infrastructure. In the recent past bicycle mechanical technology has seen significant progress, after a long period of stagnancy. A co-benefit of non-motorized transport is public health improvement.

Public Transport

Public transport by rail, tram, and bus has lower specific CO_2 emission rates than current private cars (Table 5.6), and therefore may contribute to emission reduction. Besides, it gives mobility to people who do not have access to cars and provides more capacity at a lower cost. Well-developed infrastructures and good service help to make public transport attractive.

Individual Mobility Behavior

Considering the efficiency and energy storage characteristics of different automotive drive systems, a mix of systems can be expected for the future. Given the limited storage capacities for electrical energy, electric vehicles will be applied mostly for covering short to medium distances (Fig. 7.7). As a result, combustion engines probably will remain dominant in the future for long distances where public transport or combinations with private (rented) cars should be a real alternative. Selection of transport systems will also depend on the individual needs for mobility.

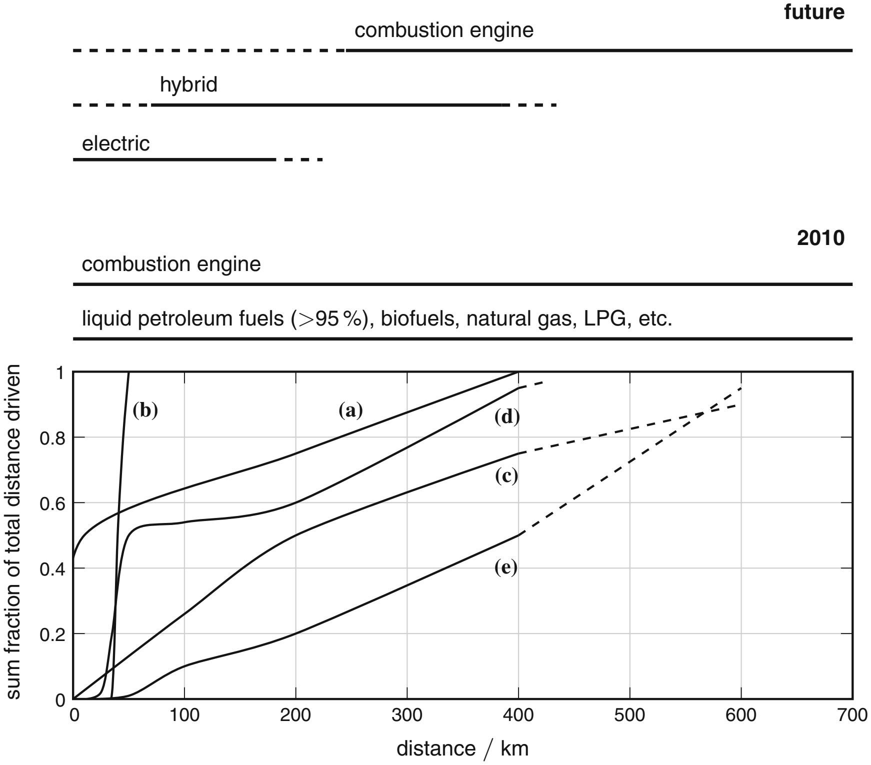


Fig. 7.7 Automobile drive systems today and in the future, as projected by car manufacturers (Steiger 2009, *top*) and characteristic driving behavior of representative individuals and the authors in 2010 (*bottom*), (*a*) city and family leisure driving, (*b*) to and from daily work, (*c*) mid- to long-distance professional driving (salesperson), (*d*) and (*e*) the authors

Overview of Technologies and Energy Carriers

An overview of conventional and future technologies for energy supply in mobile applications is shown in Table 7.7. In all applications (land-, air-, water-based applications) electricity will become more important, due to the large generation potential from renewable sources (solar, wind, and others, see Sect. 6.3).

Table 7.7 Significant technologies for energy supply in mobile and transport applications

Conventional	Future
Car (+ truck)	
– Combustion engine (piston) with petroleum fuels (Germany: natural gas $<5\,\%$, biofuels[a] $<7\,\%$)	– Electric motor with renewable electricity – Combustion engine and hybride with non-fossil fuels from biomass[b] and renewable electricity
Airplane	
– Gas turbine, piston engine with petroleum fuels	– Gas turbine, piston engine with non-fossil fuels from biomass[b] and renewable electricity
Ship, vessel	
– Combustion engine/gas turbine with petroleum fuels (natural gas)	– Combustion engine/gas turbine with non-fossil fuels from biomass[b] and renewable electricity

[a] From vegetable oil and food carbohydrates
[b] Preferably from lignocellulose, algae

7.2.4 *Bioenergy*

The use of biomass or biomass-derived fuels allows for direct substitution of fossil fuels, either in stationary combustion systems or in mobile applications (as transport fuels in car and ship engines or in gas turbines). Present technologies and potential future applications are listed in Table 7.8. Besides direct combustion, chemical or fermentative upgrading to high-value liquid or gaseous fuels appear to be attractive routes. These upgraded fuels allow for the use of present distribution infrastructures such as gas stations for liquid fuels or pipeline systems for natural gas.

In the case of upgrading, the most important feedstocks are the following (Hamelinck and Faaij 2006; Schaub and Vetter 2008; Schaub and Pabst 2011): (i) vegetable oils (converted via transesterification or hydrogenation to Diesel fuel substitutes), (ii) sugar or starch carbohydrates (converted via fermentation to ethanol as gasoline component, or to methane as a natural gas substitute), or (iii) lignocellulose (converted via thermochemical conversion to synthetic liquid or gaseous fuels or via fermentation after a saccharification/hydrolysis pretreatment). Feedstocks for (i) and (ii) are cultivated in present food-producing agricultural systems, offering opportunities for flexible integration. However, they compete with food raw materials.

Table 7.8 Technologies for using biomass as energy source

Conventional	Future
– Combustion for small-scale heat generation	– Cogeneration of electrical energy and heat
– Co-combustion with coal in medium and large capacity power plants	– Combustion – Gasification and fuel gas combustion
– Liquid transport fuels (Biodiesel, ethanol, *first generation*)	– Upgrading to gaseous and liquid fuels – Refining or chemical synthesis
– Biogas (methane) via fermentation for use in small-scale heat and electricity generation	– Fermentative or microbial conversion

Transportation fuels made from vegetable oil and sugar/starch carbohydrates are called *first generation* biofuels because their raw materials compete with food and feed applications. They are liquids in the boiling range of gasoline (ethanol) and Diesel fuel (fatty acid methyl esters (FAME) and hydrogenated vegetable oils (HVO)). They are used in their pure form or as blending components of petroleum fuels. In contrast, fuels based on lignocellulose are called *second generation* biofuels, because competition with food production can be avoided (Box 7.3). This is the case in particular if residues from agriculture, forestry, or from first generation biofuel production are used. Combinations with energy crops from agroforest systems or from microalgae cultivation can also be envisaged as feedstocks. Synthetic fuels, e.g. liquid hydrocarbons via gasification and synthesis, are known from large scale production from coal or natural gas as feedstocks. They exhibit a high flexibility in molecular composition, and can therefore be tailored to the specific combustion system (*designer fuel*). Microbial conversion of carbohydrate-containing residues to oils that can be ultimately processed to liquid hydrocarbons is another potential route to renewable high energy density fuels (Ratledge and Cohen 2008). If methane is produced as synthetic gaseous fuel, there is an advantage due to the available gas distribution system.

Processes for Biomass Conversion to Fuels

Selection of an appropriate conversion process depends on the kind of biomass feedstock to be used and on the desired product. For the production of transport fuels, Fig. 7.8 summarizes the most important conversion routes, with idealized conversion reactions in Table 7.9. The enthalpies of reaction (as well as product separation from liquid water if required) limit the energy efficiencies of the conversion process, i.e. the ratio of heating values of the product and raw material. Fuel yields per area of farmland considering the overall chain biomass cultivation-conversion are, however, dominated by photosynthetic growth of the biomass. The most significant factors here are climatic conditions (temperature, water availability) and type of plant (see Sects. 3.4 and 6.2). Values of fuel yields range between 20 GJ ha^{-1} a^{-1} (ethanol from

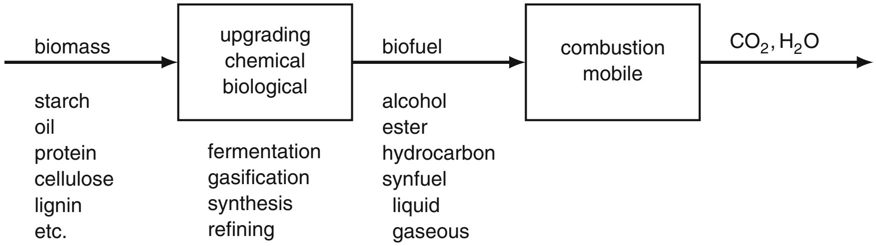


Fig. 7.8 Biomass conversion routes to transport fuels via (bio-)chemical upgrading

Table 7.9 Idealized formulation of photobiological and chemical reactions for fuel generation and related enthalpy changes (examples)

Reaction	Stoichiometry (model reaction)	$\Delta_R H^0_{298}$ per mole of C[a] kJ mol^{-1}
Photosynthesis	$6\,CO_2 + 6\,H_2O \longrightarrow C_6H_{12}O_6 + 6\,H_2O$	+479.4
Photobiological H_2O splitting (with microalgae)	$C_6H_{12}O_6 + 6\,H_2O \longrightarrow 6\,CO_2 + 12\,H_2$	+92.2
Transesterification (vegetable or algal oil)	$C_{57}H_{104}O_6 + 3\,CH_3OH \longrightarrow 3\,C_{19}H_{36}O_2 + C_3H_5(OH)_3$	+0.1
Hydrogenation	$C_{57}H_{104}O_6 + 15\,H_2 \longrightarrow 3\,C_{18}H_{38} + C_3H_8 + 6\,H_2O$	−19.2
	$C_{57}H_{104}O_6 + 6\,H_2 \longrightarrow 3\,C_{17}H_{36} + C_3H_8 + 3\,CO_2$	−8.8
Fermentation	$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2$	−23.7
	$C_6H_{12}O_6 \longrightarrow 3\,CH_4 + 3\,CO_2$	−34.3
Gasification (lignocellulose)	$C_6H_{12}O_6 \longrightarrow 6\,CO + 6\,H_2$	+89.4
Hydrocarbon synthesis	$CO + 2\,H_2 \longrightarrow CH_2 + H_2O$	−185.7

[a] Based on empirical correlation for heat of combustion, H_2O liquid

lignocellulose or FAME from jatropha) and 140 GJ ha^{-1} a^{-1} (ethanol from sugar cane in Brazil, FAME from palm oil or synthetic hydrocarbons from lignocellulose, FNR 2009), respectively between 600 and 4000 L ha^{-1} a^{-1} oil equivalent, all values for gross yields.

Box 7.3: Second Generation Biofuels

Second generation biofuels include fuels made from non-food biomass, especially residues from agriculture, forestry or residues from first generation biofuel production. As the macromolecular lignocellulosic fraction of biomass is meant to ensure mechanical and chemical stability of plants, the intended decomposition to smaller molecules is difficult. Figure 7.9 shows as basic strategies (i) enzymatic or thermal hydrolysis as pretreatment to generate smaller carbohydrate molecules for subsequent fermentation to ethanol, and (ii) thermochemical decomposition/pyrolysis with subsequent reforming and partial oxidation reactions to form synthesis gas H_2/CO. Synthesis gas then can be used as feedstock for a chemical synthesis, e.g. to form synthetic hydrocarbons (Biomass-to-Liquid, BTL). Alternative synthesis products that can be used as fuel include methanol, dimethylether, methane, and hydrogen.

The advantage of biomass conversion processes based on synthesis gas is the flexibility with respect to the kind of biomass feedstock. In the case of hydrocarbon (Fischer–Tropsch) synthesis, the final product is a high-quality Diesel fuel or kerosene. Therefore, combinations of thermochemical and fermentative conversion processes could lead to flow schemes analogous to present petroleum refineries (*biorefineries*).

Both biotechnological and thermochemical strategies are currently being developed in pilot or demonstration plants (e.g. Antizar-Ladislao and Turrion-Gomez 2008; Clariant 2015; Henrich et al. 2009; Kacelle 2015). Critical for the time being are (i) the complexity and overall cost of these biomass conversion routes, given the high performance requirements of enzymes and investment figures due to complex plant equipment schemes, and (ii) limited energy efficiency of the overall conversion with expected values of 30–45 %. With increasing oil price, however, biomass will become more competitive for transportation fuel production.

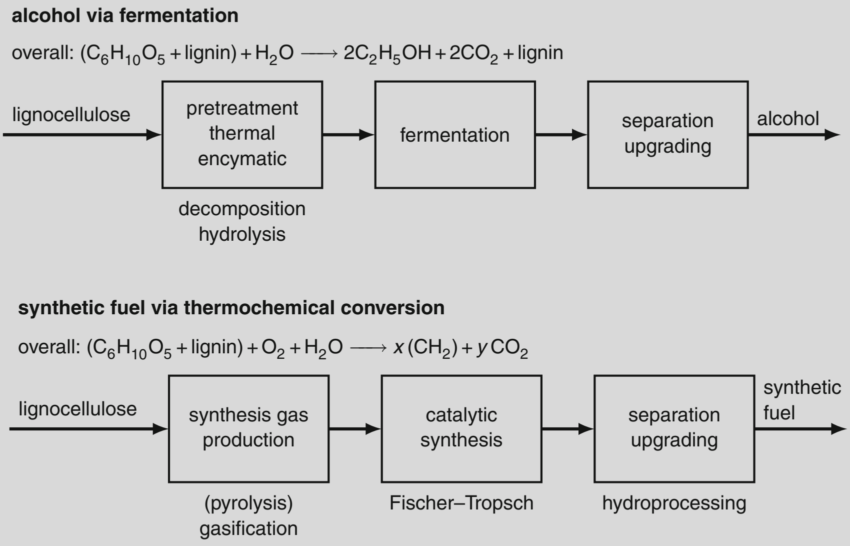


Fig. 7.9 Simplified flow diagrams of lignocellulose-to-liquid biofuel processes based on fermentation (*top*) and thermochemical gasification/synthesis (*bottom*), example Fischer–Tropsch synthesis

As for the availability of biomass raw materials and sustainability aspects, the following points regarding increased utilization of bioenergy and transportation fuels from biomass can be made:

a) Total yields are limited by net productivity of photosynthesis, land and water availability, and energy loss during conversion/upgrading, therefore, biofuels cannot simply replace petroleum as the general basis for transportation fuels. Integration of H_2 from renewable electricity can increase the yield per hectare considerably (Fig. 7.11).
b) They can contribute to CO_2 emission reduction if no significant negative effects are caused by changes in land use connected to biomass cultivation, e.g. release of carbon stored in natural reservoirs (rainforest, peat-bog etc.), or by inappropriate agricultural practice leading to excessive greenhouse gas emissions. If practiced properly, they represent an example for the transition of present non-sustainable (fossil) practice to a sustainable raw material economy.
c) Designing biomass cultivation systems and maintaining crop rotation (according to Good Agricultural Practice, GAP) must ensure a sustainable agricultural system.

Biomass utilization for supplying energy competes with direct systems for converting solar irradiation to heat or electricity (solar collectors or photovoltaic systems). Energy conversion or energy gain as criterion alone would favor solar collectors and photovoltaic systems over bioenergy generation. However, integration in rural social structures as well as handling and storage characteristics are arguments for growing biomass for energy applications.

7.2.5 Hydrogen

Hydrogen has been suggested as an energy storage medium for the production of electricity, transport fuel or heat. The prospects for a so-called hydrogen economy, however, will depend on the availability of non-fossil production at competitive cost and also on the availability of H_2 utilization technologies. The former could be based on steam reforming reactions of biomass or methane, or splitting reactions of water, e.g. using carbon-free electricity from non-fossil sources (see Table 7.10 and Sect. 7.2.6). In any H_2 production process, energy losses will occur, i.e. from an energy efficiency view this is not advantageous. The main advantage would be in the infrastructure (only one pipeline-based general system), on the side of utilization (e.g. flexible size fuel cell systems for electricity generation) and in low pollutant formation during electrochemical oxidation or combustion.

Table 7.10 Technologies for hydrogen production

Conventional	Future
(Thermo) chemical, from fossil raw materials	(Thermo) chemical, from biomass
– Steam reforming of natural gas $CH_4 + 2\,H_2O \longrightarrow 4\,H_2 + CO_2$	– Pyrolysis/gasification $CH_{1.6}O_{0.7} + 1.3\,H_2O \longrightarrow 2.1\,H_2 + CO_2$
– Partial oxidation of petroleum fractions and coal	
Electrochemical	Photo/electrochemical
	– Electrolysis with non-fossil electricity (Sect. 7.2.1)
	– Photochemical
	Biochemical
	– Fermentation
	– Photolysis (e.g. with microalgae) (Sect. 7.2.1)

7.2.6 Chemical Fuels from Electricity

With increasing amounts of electricity generated from renewable sources (wind, solar), significant fluctuations appear in the electricity system. These fluctuations include day-night cycles for solar energy and non-cyclic changes of wind speed, the latter with high rates of change and potentially longer periods of zero input. In connection with limited capacities of electrical distribution grids, this will lead to low-value or cheap electricity during times of high generation and low demand. In these excess situations, the electric energy should be converted into storable forms of energy. A variety of storage technologies are either proven (e.g. transformation to gravitational energy or pumped hydropower) or at some stage of development (pressure-volume energy of compressed air, electro-chemical storage in large scale, transformation to chemical energy, and others). Chemical fuels in general are seen as important options for medium- and long-term storage systems (Droste-Franke et al. 2012), a general flow diagram of electricity-to-fuel conversion is shown in Fig. 7.10.

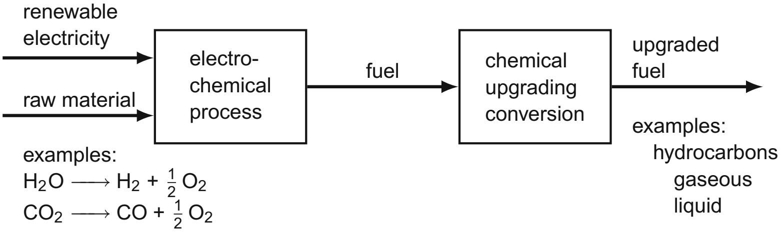


Fig. 7.10 General flow diagram of electricity conversion to chemical fuels

With respect to potential future fuels made from renewable electricity, selection of preferred energy carriers will be based on the following criteria: (i) fuel properties matching the requirements of present infrastructures for distribution and utilization (e.g. energy density, combustion, and handling properties), (ii) production costs depending on availability and price of raw materials and the required process costs for transformation/conversion, and (iii) environmental aspects, e.g. generation of pollutants and greenhouse gases during transformation and combustion (Schaub et al. 2013).

Electrolysis of water is an electrochemical technology for the production of hydrogen from water. There are various types of electrolysis cells, based on different kinds of electrolyte (alkaline, PEM (polymer electrolyte membrane), solid oxide) and electrodes. They have different characteristics with respect to module capacity, efficiency, stability, and dynamic operation. While alkaline electrolysis is commercially available on a relatively large scale, it has been announced that more dynamic and compact PEM electrolysis systems will be commercially available within a few years. The especially energy-efficient high-temperature solid oxide electrolysis is still at the research stage. Although electrolysis cells presently have high specific investment figures, there are positive expectations for cost reduction, high rates of load change, and operability (Smolinka 2009). Conversion of hydrogen to upgraded fuels will be desired according to the first criterion mentioned above, i.e. for achieving desired fuel properties. Liquid or gaseous hydrocarbons are examples where hydrogen can be integrated in chemical upgrading processes, leading to an overall electricity-to-fuel process (Fig. 7.11). In the case of substitute natural gas, SNG, based on methane (*power-to-gas*), or liquid hydrocarbon fuels like kerosene, gasoline, Diesel (*power-to-liquid*), integration in present infrastructures would be easy. However, any upgrading process has internal energy demands, therefore, for energy efficiency reasons direct utilization of hydrogen would be preferable.

If hydrogen is to be converted to hydrocarbons, different carbon sources can be used (Schaub et al. 2013). (i) In the case of fossil raw materials, yields per feedstock can be increased and fossil CO_2 emissions decreased since fossil resources for

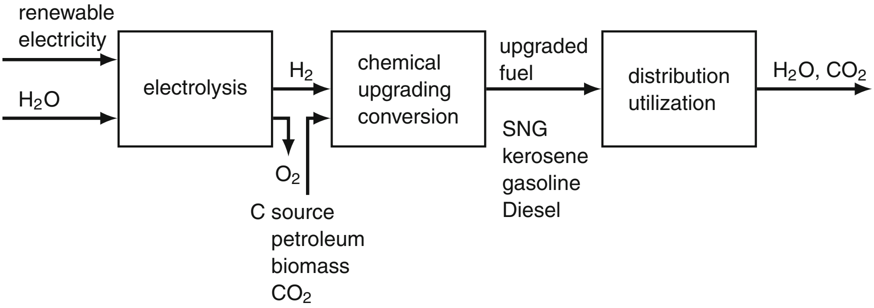


Fig. 7.11 Flow diagram for production of hydrocarbon fuels (gaseous or liquid) from renewable electricity via hydrogen, *SNG* substitute natural gas

H_2 production can be avoided. (ii) In the case of biomass conversion to synfuels, product yield per biomass or hectare can be increased, and in the case of vegetable oil hydrogenation, fossil resources for H_2 production can be avoided (Schaub et al. 2014). (iii) With CO_2 as feedstock, no gasification step is needed, however, the lowest hydrocarbon product yields per unit H_2 are achieved, owing to the high oxidation value of CO_2. Research topics related to electricity-to-fuels are: cost reduction and upscaling of electrolysis, system development with respect to availability of fluctuating electricity (installation size, time pattern, location), and dynamic behavior resulting from electric power fluctuations. Renewable electricity can be converted in excess situations not only to fuels but also used to generate heat and thus replace combustible fuels. In addition, electricity can be integrated in the production of bulk chemicals (e.g. ammonia, methanol, *power-to-chemicals*).

7.3 Climate Engineering

The idea to modify the global climate is surprisingly old. Jules Verne described in his 1889 novel *Sans dessus dessous* (Verne 1889), which was later published in English under the titles *Topsy-Turvy* and *The Purchase of the North Pole*, the fantastic plan to change the position of the Earth's axis by launching a heavy projectile horizontally to the south with a giant cannon. The recoil would displace the center line of the Earth and create a new axis perpendicular to the direction of the Earth's orbit. As a result, it was believed that the Arctic ice cap would melt and allow for the exploitation of large coal reserves supposedly present in that region. Fortunately the plan failed, since a successful shooting of the cannon would have caused sudden disastrous movements of the liquid mass of the ocean, presumably with millions of fatalities.

Today, the term *climate engineering* or *geoengineering* refers to proposed methods for manipulating the Earth's climate to counteract the warming effects of anthropogenic greenhouse gas emissions. Besides the truly exotic plan to reduce the incoming solar radiation far outside the atmosphere by launching a myriad of small free-flying, reflective disks into an orbit aligned with the Sun (Angel 2006), all suggestions are targeted at either increasing the Earth's albedo or at removing the most important anthropogenic greenhouse gas CO_2 from the atmosphere.

These proposals can be subdivided into methods that increase the albedo of either the atmosphere or land surface, and methods that enhance the ability of land or the ocean for carbon dioxide storage (Table 7.11). A rise in atmospheric albedo could be reached by depositing aerosols to the stratosphere or by stimulating cloud formation. The albedo of the land may be increased by covering wasteland with reflective surfaces or through growth of tailored vegetation. Afforestation of reforestation are obvious means to increase the capacity of the biosphere for CO_2 uptake and to sequester carbon. Other possible means of decreasing the carbon dioxide content of the atmosphere are the removal of biomass from the carbon cycle by carbonization through pyrolysis in the absence of oxygen, or burial in oxidation-proof layers of the soil. Another option for enhancing the carbon sink is chemical scrubbing of CO_2

Table 7.11 Proposed climate engineering methods

Options	Methods	Scenarios
Increased atmospheric albedo	Stratospheric aerosols	Delivery of particles with about 5 Mt a^{-1} S e.g. by aircraft (Crutzen 2006)
	Mechanical cloud seeding	(a) Seeding clouds in the marine boundary layer with fine seawater spray ($d = 1\,\mu\text{m}$, $F_V = 30\,\text{m}^3\,\text{s}^{-1}$, Latham et al. (2008)), (b) seeding of cirrus clouds in higher atmospheric regions to reduce radiative forcing (Mitchell and Rasch 2009)
	Biological cloud seeding	Iron fertilization of the ocean to enhance dimethyl sulfide formation and cloud generation (Wingenter et al. 2007), see also Sect. 4.5
Increased surface albedo	Surface coverage	Albedo increase through application of reflective surface in deserts (2 % of Earth's surface required, Lenton and Vaughan (2009))
	Tailored vegetation	Growth of plants with increased albedo in grassland and savannah (Hamwey 2007)
Increased land CO_2 sink	Afforestation	Removal of up to 120 Gt C by 2035 through reforestation and afforestation (Read 2008)
	Biomass carbonization/burial	(a) Production of charcoal from biomass with removal of up to 52 Gt C by 2060 (Lehmann et al. 2006), (b) fixation of biomass in oxidation-proof environment (Kreysa 2009)
	CO_2 capture and storage	Carbon dioxide scrubbing from large point sources and disposal in geological formations (Breeze 2008)
Increased ocean CO_2 sink	Fertilizer addition	Enhanced oceanic biomass production through addition of phosphorus, nitrogen, or iron fertilizer (Lenton and Vaughan 2009)
	Upwelling	Fertilization by artificial upwelling flux of nutrient-rich water from lower ocean (Lovelock and Rapley 2007)
	Carbonate addition	Addition of finely ground $CaCO_3$ to increase alkalinity of ocean (Lenton and Vaughan 2009)

from point sources, such as thermal power plants followed by storage, e.g. in geological formations. Finally, there are suggestions to enlarge the ocean CO_2 sink by fertilizing the oceanic biomass or through addition of alkaline substances.

Only a few of these proposals have been tested experimentally for their feasibility and efficiency for climate manipulation. Several iron fertilization experiments have been carried out in the Southern Ocean to stimulate the growth of iron-limited phytoplankton with the idea of subsequent sinking of organic matter and ultimately sequestration of atmospheric carbon dioxide in the deep sea and sediments. Although phytoplankton blooms could be produced in most of these experiments, it remains unclear if a significant effect on the atmospheric carbon dioxide content could be achieved without negative side effects on the ocean and atmosphere (Smetacek and Naqvi 2008). Carbon capture and storage (CCS) from coal-fired power plants has been recently studied by several companies on a pilot scale. Although chemical CO_2 scrubbing has already been proven to be a reliable technology on a relatively large scale, questions remain if CCS will be able to cope with increasing atmospheric carbon dioxide concentrations. One problem is related to the high energy demand for carbon dioxide capture, which may reduce the efficiency of electrical energy generation by as much as 20 %. A second unresolved problem is that the sequestered carbon dioxide must remain in suitable geologic formations for very long times if this strategy is to be effective.

Lenton and Vaughan (2009) have compared the radiative forcing potential of several climate engineering proposals and showed that only very few techniques have the potential to counteract the expected rise in anthropogenic greenhouse gas emissions. Among these are stratospheric aerosol injections and mechanical enhancement of marine cloud albedo. However, these options are risky because they have to be continually operated and if a sudden termination were necessary for whatever reason, extremely rapid global warming could result. Methods altering the carbon cycle appear to carry less risk. However, they could be in conflict with food production and/or the preservation of natural ecosystems.

7.4 Individual Living Conditions and Lifestyles

Absolute values of anthropogenic energy and material flows can be easily converted into average values per-capita. These specific values give an indication of the material or energy intensity in a given country. Looking at CO_2 as an example, per-capita values reflect the fossil contribution to the national energy supply and, as fossil fuel contributions today are dominant in most cases, indicate the material standard of living. These specific values are helpful for individuals to assess their own way of living and compare it with living conditions in other countries or with other lifestyles.

As an example, Table 7.12 gives values for fossil CO_2 emissions per year of a representative 3-person family (middle class) in a highly industrialized and in a less-developed country. Resulting total per-capita emission rates are 10.4 and 1.0 $\mathrm{t\,cap^{-1}\,a^{-1}}$ CO_2 respectively, showing a factor of about 10. In all sectors of the

Table 7.12 Example fossil CO_2 emission rates of 3-person family (in $t\,a^{-1}$) in industrialized country with developed infrastructure and less developed country with limited infrastructure (rural setting), based on Anon (2007), see national average values in Fig. 5.22

	Fossil CO_2 emission rate			
	Industrialized country		Less-developed country	
	$t\,a^{-1}$	$t\,a^{-1}\,cap^{-1}$	$t\,a^{-1}$	$t\,a^{-1}\,cap^{-1}$
Electricity	2.7	0.9	0.6	0.2
Heating, cooking, warm water	7.2	2.4	0.3	0.1
Mobility				
Car	4.0	1.3	0	0
Airplane	1.2	0.4	0	0
Train, bus, metro etc.	0.6	0.2	1.2	0.4
Food	4.5	1.5	0.2	0.1
Goods	8.1	2.7	0.3	0.1
Infrastructure	3.0	1.0	0.3	0.1
Total	31.3	10.4	2.9	1.0

economy, there are significant differences, with values of zero for car and airplane mobility in less-developed country and the largest factor (27) for the production and distribution of consumer goods. Underlying assumptions are listed in Table 7.13. Specific CO_2 emission per unit of electricity, for example, reflects the electricity generation mix assumed (coal/nuclear/renewables/natural gas).

Fossil CO_2 emissions related to food are closely linked to the consumption of meat. Actual consumption values in industrialized countries are in the range 50–120 $kg\,cap^{-1}\,a^{-1}$ and lead to CO_2 emissions similar to those for mobility in cars. This is due to the loss in food energy when agricultural crops are fed to livestock in order to produce meat (approx. 90 % loss). In Germany, as an example, average meat consumption is presently about 100 $kg\,cap^{-1}\,a^{-1}$, with fodder crops being imported to a significant extent from South America (about 15–20 % of total demand).

A simple estimation procedure for assessing individual lifestyles – related to individual mobility and heating of private living space – is presented in Box 7.4. This estimation is helpful if individuals want to have a critical view of their own way of living or of other desired lifestyles. Values of individual energy and CO_2 emission flow rates can be easily calculated with the data sheets presented in Tables 7.15 and 7.16, based on the approach and definitions given in Table 7.14.

Table 7.13 Assumptions used in example CO_2 emission estimates given in Table 7.12, *source* Anon (2007), modified

	Family in industrialized country Parents, 1 child, one-family house 120 m^2	Family in less-developed country Parents, 1 child, farmer in rural setting, with access to electricity
Electricity	4500 $kWh\,a^{-1}$ 0.6 $kg\,kWh^{-1}$ CO_2	600 $kWh\,a^{-1}$ 1.0 $kg\,kWh^{-1}$ CO_2
Heating, cooking, Warm water	Fuel oil 2400 $L\,a^{-1}$ 3 $kg\,L^{-1}$ CO_2	Only cooking Natural gas 225 $kg\,a^{-1}$ 1.5 $kg\,kg^{-1}$ CO_2
Mobility		
Car	2 cars 23 500 $km\,a^{-1}$ 0.08 $L\,km^{-1}$ 2.33 $kg\,L^{-1}$ CO_2	No car
Airplane	3000 $km\,cap^{-1}\,a^{-1}$ 0.133 $kg\,km^{-1}$ CO_2	No flights
Train, bus, metro etc.	2450 $km\,cap^{-1}\,a^{-1}$ 0.07 $kg\,km^{-1}$ CO_2	2000 $km\,cap^{-1}\,a^{-1}$ 0.2 $kg\,km^{-1}$ CO_2
Food	With 60 $kg\,a^{-1}$ meat 1.5 $t\,cap^{-1}\,a^{-1}$ CO_2[a]	With 3 $kg\,a^{-1}$ meat 0.075 $t\,cap^{-1}\,a^{-1}$ CO_2[a]
Goods	For production/distribution of goods	
Infrastructure	Public buildings, lighting, police etc.	
	1 $t\,cap^{-1}\,a^{-1}$ CO_2	0.1 $t\,cap^{-1}\,a^{-1}$ CO_2

[a] fossil CO_2 emissions caused by additional crop requirements for feeding livestock (energy efficiency appr. 10 %)

Box 7.4: Personal Energy Demand and CO_2 Footprint – Example Calculations for Readers

The following calculation procedure allows a reader to calculate her/his personal energy demand and footprint of fossil CO_2 emission rates related to (i) individual mobility and (ii) heating of private living space. Other sectors are more complex to consider because indirect effects and characteristics of industrial infrastructure must be taken into account (production and consumption of goods, food production, and infrastructure). Related values for orientation can be seen in Tables 7.12 and 7.13. Data sheets are presented in two tables that will allow the reader to enter personal values and to carry out the calculation procedure for individual energy demand (Table 7.15) and fossil CO_2 emission rate values (Table 7.16). Table 7.14 gives an outline of the approach and definitions used.

Table 7.14 Approach and definitions for CO_2 footprint estimation

Estimates for end energy demand and fossil CO_2 emissions per capita and year	
a) Individual mobility	– Correlates with kind of vehicle (automobile, airplane, train, 2-wheel vehicle) – Kind of drive system (for automobiles), fuel economy, kind of fuel (including energy demand for fuel production from raw materials) – Distance ($\mathrm{km\,cap^{-1}\,a^{-1}}$) – Different fractions of seats occupied assumed in private cars (1.7 persons per car), airplanes (55 %), trains (50 %) as typical average values (to be adjusted if needed) – Fossil CO_2 emissions related to electricity generation as specific values in $\mathrm{kg\,kWh^{-1}}$ assumed as representing today's electricity generation mix in Germany or idealized case of renewable electricity (to be adjusted if needed) – Specific fossil CO_2 emission values of fuels for internal combustion engines in $\mathrm{kg\,GJ^{-1}}$ assumed on the basis of higher heating value and combustion stoichiometry, biofuels idealized with zero fossil CO_2 generation – Synthetic Diesel fuels (*synDiesel*) and H_2 from natural gas include fossil CO_2 generation during chemical conversion of raw material to fuel
b) Heating of private living space	– Correlates with specific area of living space ($\mathrm{m^2\,cap^{-1}}$), energy standard of building, according to German standards – Assumed climate: Central Western Europe – Assumed heating fuel: natural gas, petroleum fuel oil, biofuels/solar – Electricity demand in passive house for forced air exchange not included – Specific fossil CO_2 emission values of fuels assumed as in individual mobility section, see (a), biofuel (e.g. wood)/solar heat collectors idealized with zero fossil CO_2 generation

Various case studies were carried out in a university course presenting the topic of the present book. The results indicate characteristic features of four different example lifestyles, which all refer to today's conditions in an industrialized country, as mentioned in Tables 7.12 and 7.13. All values can be compared to the actual personal footprint of fossil CO_2 in Germany (about $10\,\mathrm{t\,cap^{-1}\,a^{-1}}$).

Table 7.15 Data sheet for estimation of individual end energy demand for mobility and heating of residential space in kW cap^{-1}, for comparison see Figs. 5.12 and 5.13 and Box 5.2

Mobility				
....	km cap^{-1} a^{-1}	car[a]		
		Internal combustion engine[d]		
		☐ 3 L per 100 km	×0.020 × 10^{-3} kW a km^{-1}	.... kW cap^{-1}
		☐ 8 L per 100 km	×0.054 × 10^{-3} kW a km^{-1}	.... kW cap^{-1}
		☐ 15 L per 100 km	×0.101 × 10^{-3} kW a km^{-1}	.... kW cap^{-1}
		Electric drive system	×0.035 × 10^{-3} kW a km^{-1}	.... kW cap^{-1}
....	km cap^{-1} a^{-1}	Airplane[b]	×0.054 × 10^{-3} kW a km^{-1}	.... kW cap^{-1}
....	km cap^{-1} a^{-1}	Train[c]	×0.027 × 10^{-3} kW a km^{-1}	.... kW cap^{-1}
	Sum mobility			.... kW cap^{-1}
Heating, residential				
....	m^2	Area of living space		
		☐ Average[e]	×0.025 kW m^{-2}	.... kW cap^{-1}
		☐ New building[e]	×0.008 kW m^{-2}	.... kW cap^{-1}
		☐ Passive house	×0.0015 kW m^{-2}	.... kW cap^{-1}
	Sum heating			.... kW cap^{-1}
	Sum mobility and heating			.... kW cap^{-1}

[a] 1.7 persons per car, average
[b] 55 % of seats occupied
[c] 50 % of seats occupied
[d] Hydrocarbon equivalent (Diesel or gasoline)
[e] Germany 2002

1. The personal CO_2 footprint of an example couple or family with very high income (*rich and global*), both adults devoted to their work in international companies/institutions, without money limitations, is in the range 60–90 t cap^{-1} a^{-1} of fossil CO_2. Significant features of their lifestyle are: two or more apartments/houses in different locations with average energy standard, frequent travelling with long-distance flights and large-sized cars, average to high meat consumption, and high standard concerning consumer goods.
2. An example person with high middle class income without special commitment (*happy-go-lucky*) has a personal CO_2 footprint in the range 15–25 t cap^{-1} a^{-1}. Features of this lifestyle include: spacious apartment/house, car is large with high fuel consumption (potentially SUV), frequent holiday and weekend travel preferably with airplane or car, considerable meat demand, and consumer good orientation.
3. An example person of a medium-income family in Germany, committed to sustainable lifestyle experiments and energy saving, has a personal CO_2 footprint in the range 1–4 t cap^{-1} a^{-1} (*committed and regional*). Features of this lifestyle are: new house built with passive standard or apartment building with highest energy standard, heating with ambient heat and electric

heat pump or district heating, small car with biofuel or renewable electricity, family holidays with travel to regional locations (e.g. Alps, Baltic Sea), preferably by train, low or no meat consumption and very low consumer goods orientation.

4. An example student at a German University may have a personal CO_2 footprint today in the range 1–15 t cap^{-1} a^{-1}, strongly depending on the amount of financial support and on personal value orientation (*student life*). Features of this lifestyle are: small living space in student dormitory or shared apartment, limited availability of money and leisure time for travelling and food.

Table 7.16 Data sheet for estimation of personal footprint of CO_2 emission rate related to individual mobility and to heating of residential living space, values for personal energy demand from Table 7.15, fossil CO_2 emission from fuel combustion and from fuel (or electricity) production/upgrading from raw material/primary energy source

Mobility			
....	kW cap^{-1} car (from Table 7.15) with fuel		
	☐ Liquid petroleum fuel (Diesel or gasoline)	×3.1 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
	☐ SynDiesel from natural gas	×3.4 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
	☐ Natural gas	×2.0 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
	☐ H_2 from natural gas	×2.9 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
	☐ SynDiesel from biomass	×0.0 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
....	kW cap^{-1} car (from Table 7.15) with electric drive system		
	☐ Electric mix Germany 2010[a]	×5.2 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
	☐ Electric renewable[b]	×0.0 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
....	kW cap^{-1} Airplane		
	☐ Kerosene from petroleum	×3.1 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
....	kW cap^{-1} train		
	☐ Electric mix Germany 2010[a]	×5.2 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
	☐ Electric renewable[b]	×0.0 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
	Sum mobility		.... t cap^{-1} a^{-1}
Heating, residential			
....	kW cap^{-1} heat (from Table 7.15) with heat source		
	☐ Fuel oil EL	×3.1 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
	☐ Natural gas	×2.0 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
	☐ Biofuel/solar	×0.0 t kW^{-1} a^{-1}	.... t cap^{-1} a^{-1}
	Sum residential		.... t cap^{-1} a^{-1}
	Total sum		.... t cap^{-1} a^{-1}

For resulting values see Fig. 5.22 and Table 7.12

[a] 0.6 kg kWh^{-1}

[b] 0.0 kg kWh^{-1}

7.5 Global CO_2 Emission and Atmospheric Carbon Inventory Scenarios

A wide variety of climate change projections indicate that the continued release of fossil carbon into the atmosphere as CO_2 and CH_4 at current or above current rates would cause further warming (IPCC 2007d). It would induce changes in the global climate system during the 21st century that would most likely be larger than those observed during the 20th century. In a joint effort by many mathematical modeling groups worldwide, climate change projections are made based on different kinds of global climate models (Sect. 3.5). Case studies for different scenario conditions show a range of potential future developments.

The most significant variable in climate projection case studies is the emission rate of fossil CO_2 from the utilization of petroleum, coal and natural gas, and of other relevant components such as aerosols, as assumed during the 21st century. In addition, assumptions are made about the demographic and economic development in industrial, transition and developing countries, and – very important – about political success in structural changes of the energy supply and utilization sectors. In 2000, the IPCC published a Special Report on Emission Scenarios SRES (IPCC 2000), with about 40 different scenarios. The extreme cases with the highest/lowest fossil CO_2 emissions are based on emission rates of 29 $\mathrm{Gt\,a^{-1}}$ (A1FI) and 5 $\mathrm{Gt\,a^{-1}}$ (B1) in 2100 and lead to atmospheric CO_2 concentrations of 550–950 ppm, to a range of temperature increase of 1.1–6.4 K, and to a global average sea level rise of 18–59 cm in 2100. More recent IPCC reports discuss further details of mid- and long-term scenarios (IPCC 2007d, 2013).

Two example results are shown in Fig. 7.12 (IPCC 2007d, p. 803). Scenario A1B stands for *rapid economic growth and balance across all energy sources* and reaches a maximum fossil carbon emission rate of 17 $\mathrm{Gt\,a^{-1}}$ (equivalent to 62 $\mathrm{Gt\,a^{-1}}$ CO_2) in 2050. The resulting CO_2 concentration of around 700 ppm at the end of the 21st century leads to a temperature increase of 2.8 K, as compared to the year 2000. The second example scenario B1 stands for *convergent world, rapid change in economic structures toward a service, information economy and reductions in material intensity*. Here, the maximum fossil carbon emission rate is reached in 2050 at about 12 $\mathrm{Gt\,a^{-1}}$ (equivalent to 44 $\mathrm{Gt\,a^{-1}}$ CO_2). Corresponding CO_2 concentrations and temperature increase in 2100 are about 600 ppm and 1.8 K, respectively. These two examples demonstrate different successes in decreasing CO_2 emissions and stabilizing the global carbon cycle.

As a consequence of global climate change, various effects on regional conditions are emerging, depending on the geographic location in each case. Information is available and scientific assessment is ongoing about what future impacts will look like in different regions, for example as discussed in IPCC (2007e, 2013). Magnitudes of impacts are being estimated systematically for a range of possible increases in global average temperature.

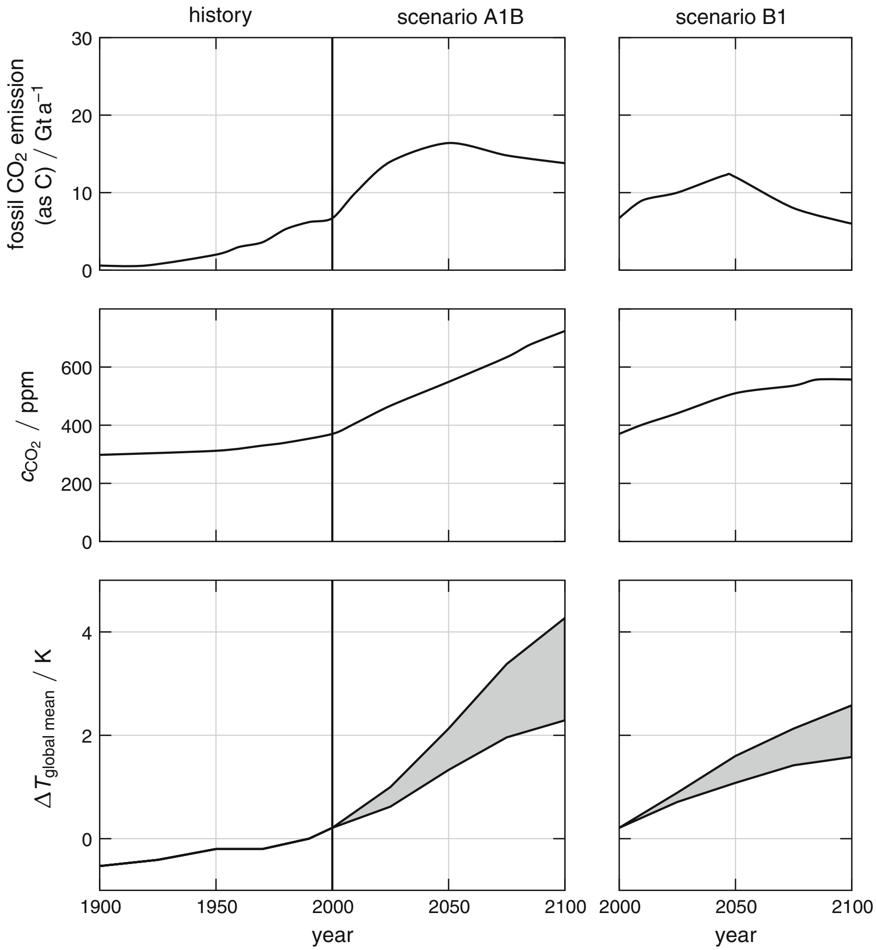


Fig. 7.12 Case studies with global climate model for different emission scenarios, two selected examples, historical data smoothed, after: IPCC (2007d, p. 803), *A1B* rapid economic growth, balance across all energy sources, *B1* convergent world, rapid change in economic structures toward a service and information economy, reductions in material intensity

As an example, Africa is one of the most vulnerable continents to climate variations because of multiple stresses and low adaptive capacity. In particular, countries in Central Africa exhibit high vulnerabilities according to the following indices (Maplecroft 2010): (i) economy (ii) resource security, (iii) ecosystems, (iv) poverty, development and health (v) population, settlement and infrastructure, (vi) institutions, governance and social capital.

Small islands, either located in the tropics or at higher latitudes, are especially vulnerable to the effects of climate change, in particular to sea-level rise and extreme weather events (storm surge, inundation). This is due to the fact that vital infrastructures, settlements, and facilities for economic activities are located in coastal areas at low altitudes.

Outline for Climate Negotiations

A scientific committee reporting to the German government presented general guidelines for negotiating future UN climate agreements, following the Kyoto Protocol (Graßl et al. 2003). Recommendations concentrate (i) on strategies and potentials for CO_2 emissions reduction and (ii) on efficient ways to preserve biological carbon reservoirs and sinks in the biogeosphere. The underlying assumption emphasizes that global average temperature should increase no more than 2 K compared to preindustrial times and the rate of increase should remain below 0.2 K per decade. Scenarios treated with mathematical models are based on the scenario systematization developed by the Intergovernmental Panel on Climate Change (IPCC 2007d). According to the recommended measures, research and development activities should be increased in order to supply the technologies required.

CO_2 Emission Reduction

General directions recommended include: (i) to improve energy efficiency in primary energy conversion and end energy utilization processes, (ii) to change the structure of primary energy supply by enlarging the use of renewable or carbon-poor sources, and (iii) to apply CO_2 sequestration in geological formations as a transition technology in the near future.

As a general concept, *decrease and convergence* (of fossil CO_2 emissions) is proposed. Per-capita emissions of CO_2, seen as emission rights per capita, should – within a limited time frame – converge to similar values in all countries. Accordingly, today's industrial countries have to decrease emissions, whereas developing countries first can increase, and later also decrease their CO_2 emissions. The set time frame should allow for smooth changes of national and global economies. A basic measure for practical implication should be a trading system for CO_2 emissions. Resulting economic difficulties in developing countries should be alleviated by financial aid programs by the international community. An example case study with resulting per-capita emissions of different regions is shown in Fig. 7.13 for a time frame up to 2100.

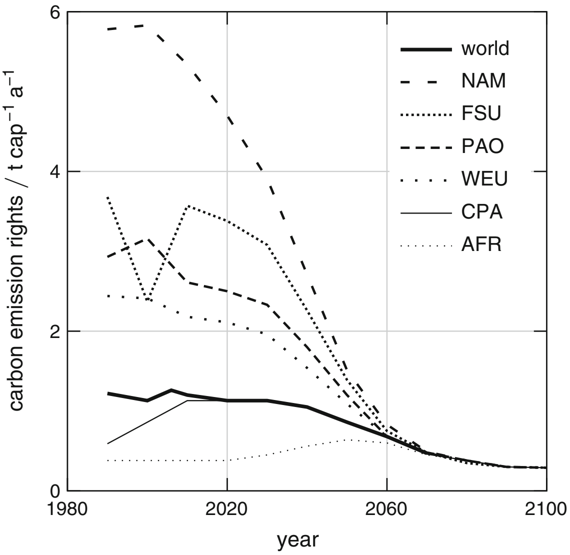


Fig. 7.13 Scenarios of fossil CO_2 emissions per-capita and year (values as carbon) in different world regions, based on the proposed concept of convergence of emission rights until 2100, after: Nakicenovic (2003) reference in Graßl et al. (2003), *NAM* North America (USA, Canada), *FSU* countries of former Soviet Union, *PAO* Pacific OECD countries (Japan, New Zealand, Australia), *WEU* Western Europe, *CPA* state economies Asia and China, *AFR* Africa south of Sahara

Preservation of Terrestrial Ecosystems

General directions recommended include: (i) to develop a better understanding of the global carbon cycle and quantify in detail actual carbon flows for future monitoring of carbon reservoirs (*full carbon accounting*), and (ii) setting goals for preserving endangered natural carbon reservoirs, in particular primary forest, swamp areas, or grassland, see Sect. 3.4.

Today's state of knowledge already allows for a simple comparison of carbon reservoirs, as treated in Chaps. 4 and 6. The magnitude of known fossil resources indicates that even limited fractions utilized as energy source in the future would release fossil carbon into the atmosphere in quantities which would alter its present inventory significantly. The sum of conventional fossil reserves known today exceeds the carbon inventory of the atmosphere significantly, as can be seen from Fig. 7.14. This appears to be a strong indication of the relevance of human industrial activities with fossil carbon utilization for the carbon system on Earth. Depletion or shortage of fossil energy materials will not be what will limit their utilization in the foreseeable future. Only international negotiation and agreement to use renewable energy sources instead will help the global society to keep greenhouse gas inventories in the atmosphere below the critical values in order to preserve acceptable climate conditions.

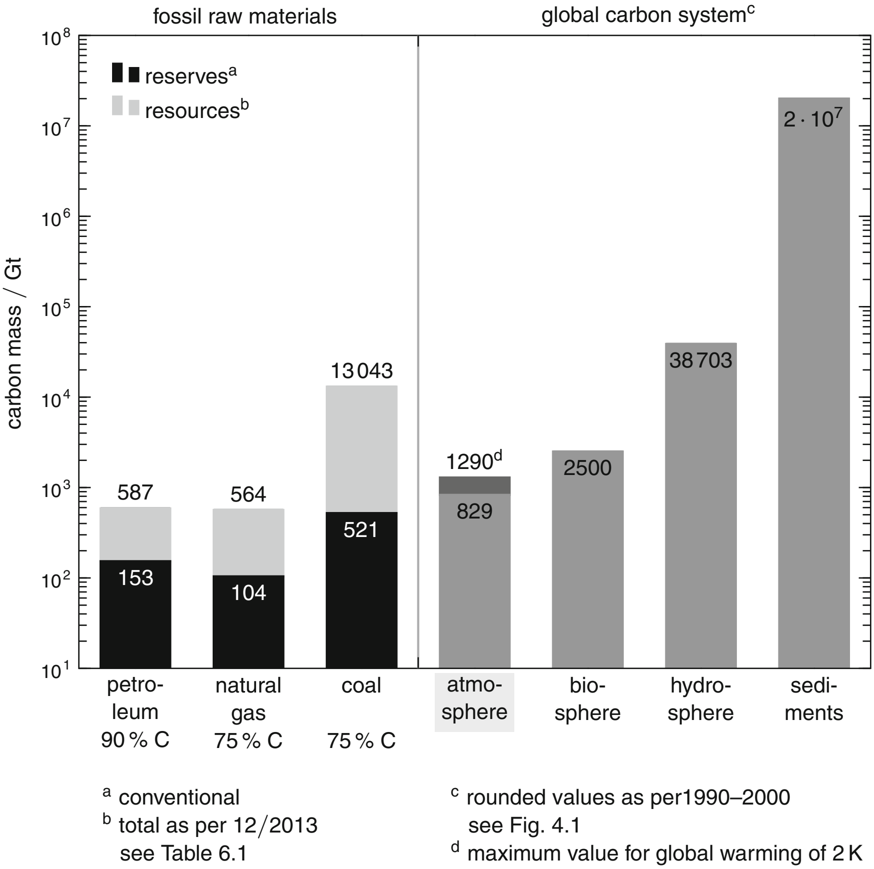


Fig. 7.14 Total carbon inventories of fossil reserves and resources (*left*, definitions and values in Chap. 6) and main global carbon reservoirs (*right*, definitions and values in Chap. 4), with maximum allowable carbon value in the atmosphere, estimated with global climate models for a global warming of 2 K

During the Climate Conference in December 2015 in Paris (Conference of the Parties COP21), an agreement was reached between 195 countries, that will follow the Kyoto Protocol. Keeping the increase of the average global temperature below 2 K or preferably below 1.5 K during the 21st century was set as the common goal. In order to achieve this, a worldwide transition to an energy system based on renewable instead of fossil sources is needed. Given the different boundary conditions (geographic, economic, cultural, etc.), each country must define its best technology mix and path for this transition. General terms for financial compensation were defined, helping the poorer countries and those with greater damage risks to spend the required investments. A control mechanism was agreed, including critical assessment of the progress made every five years.

7.6 Transition of the Energy System – Example Germany (Energiewende)

After many years of discussion about the risks of nuclear energy and environmental footprints of energy sources, the nuclear incident in Fukushima 2011 led to a new energy supply concept for Germany. As a consequence, a transformation of the German energy system by 2050 was recently claimed as a political aim, with the goal of providing energy from mainly renewable energy sources. The resulting German energy transition (*Energiewende*) is an example of an ambitious integrated transformation project because it depends not only on technological changes, but also on social and institutional change. The political decision in 2011 for a comprehensive *energy transition* made Germany a pioneer case for such a transformation project (Schneidewind et al. 2013). The targets of this transition project were anticipated in a report by the German Advisory Council on Global Change (WBGU 2011) and addressed (i) significant reductions of fossil CO_2 emissions, (ii) efficiency increases in energy conversion and utilization, and (iii) a decrease in primary energy demand.

The energy supply envisaged for a non-fossil and non-nuclear energy future is visualized with the energy flow diagram in Fig. 7.15. Primary energy supply should be based mainly on renewable sources, using wind and solar energy, given the high supply potentials and, to a lesser extent, on hydro power and biomass. Total primary energy demand should be reduced from 5.4 to 2 kW cap^{-1} (*2000 Watt Society*). As renewable energy sources will primarily lead to electricity generation, chemical

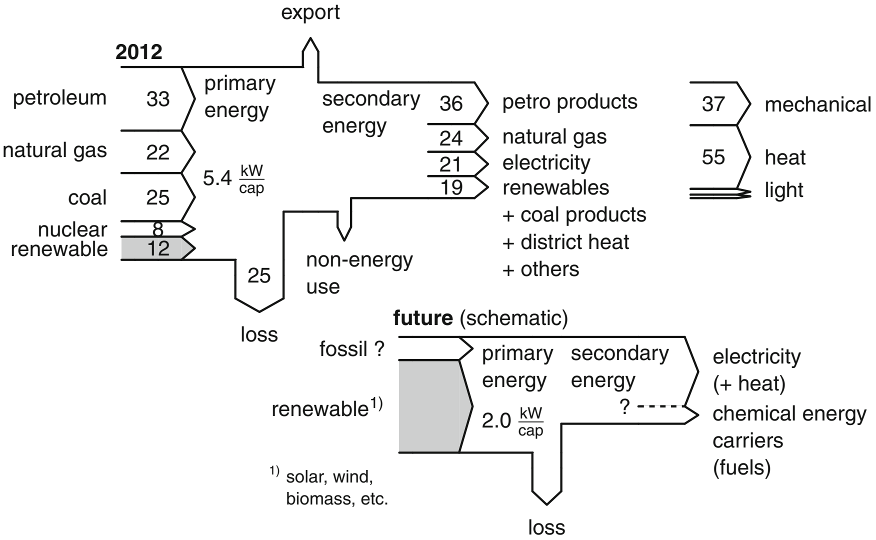


Fig. 7.15 Energy flow distribution in Germany 2012 and orientation for future development, *gray* renewable contribution, *basis* (Energiebilanzen 2014; UBA 2014; WBGU 2011)

energy carriers will only be used in cases, where the specific advantages are important (energy density, storage, and handling properties), e.g. for mobile applications. Therefore, conversion of electrical energy into chemical energy carriers may become important in the future (see Sect. 7.2.6).

Obviously, the defined goals cannot be reached by implementing technological energy efficiency measures alone. In addition, success of the transition of the energy system also depends on changes in energy consumption and individual behavior which is connected to social and cultural practices. Therefore, the transition process envisaged has to address four dimensions (Schneidewind et al. 2013):

a) technologies and infrastructures (technological perspective),
b) financial capital (economic perspective),
c) institutions/policies (institutional perspective),
d) cultural change/consumer behavior (cultural perspective).

All technological, economic and institutional processes and dynamics are embedded in the culture of a society. Therefore, the cultural changes are possibly the most fundamental changes that are required. The overall success of the German energy transition will also depend on substantial energy savings (in addition to technological efficiency improvements) via breaking routines and habits, thus facilitating behavior that is compatible with new norms and values. This is supported by institutional and political framing. What is required is the willingness to assume societal responsibility, increase significance of post-material values, and to stay the course in a long-term process.

An analogy can be seen to some extent in the historical situation during the 1970 and 1980s, when in Germany the transition to a better understanding and practice of environmental protection occurred. Detrimental environmental effects of industrialization on a local and regional scale became obvious (e.g. *acid rain*), people noticed that preservation of the natural environment is an important aspect of welfare and prosperity, deserving attention and economic expenses. The resulting process of developing and implementing technologies for cleaning off-gases, waste water etc. was successful and in the end also economically advantageous.

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Chapter 8
Conclusions

The Earth is a complex system and a complete understanding of the interactions of all processes taking place has not yet been achieved. However, we believe that a number of fundamental constraints, limitations, and guidelines for future development can be derived from the process engineering approach presented in this book. As a result, the following conclusions are based on the view that humans should avoid significant perturbations of natural cycles in the biogeosphere. They are comprised of some facts regarding natural and anthropogenic flows in the biogeosphere as well as important aspects of sustainable global development.

1. The Earth is a closed system with almost no material exchange with space and continuous flow of radiative energy from the Sun as a driver of (bio)chemical and physical processes in the biogeosphere. Dynamic interactions of these processes together with complex feedbacks determine the material cycles and energy transformations on Earth.
2. The overall energy balance of the Earth is influenced by the reflective properties of the atmosphere and the surface (albedo) as well as by the ability of atmospheric components to interact with infrared radiation emitted from Earth's surface (greenhouse effect), with both processes being strongly coupled. The extension of Earth's ice caps has a major influence on the average global surface temperature. The structure of the underlying energy balance reveals that relatively minor fluctuations of global ice coverage may lead to self-enhancing processes with drastic results. Although water vapor is the component with the strongest contribution to the greenhouse effect, its atmospheric concentration is directly linked to temperature. This is why other atmospheric trace gases such as carbon dioxide (and, to a lesser extent, methane and nitrous oxide) also play a decisive role for the greenhouse effect.
3. Chemical transformations in the closed Earth system proceed in interlinked cycles. Subsystems of the Earth such as atmosphere, ocean, biosphere, and sediments, contain different amounts of chemical species that are exchanged by material flows – often connected to energy flows – with other subsystems. In

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addition to inorganic processes, the formation and further evolution of life has been the most important factor for the present global material cycles.

4. Photosynthesis has caused significant transformations of the atmosphere during Earth's history. Photosynthesis removed large amounts of CO_2 from the atmosphere in earlier times, thus generating favorable greenhouse conditions for the evolution of life. Parts of the biomass formed by photosynthesis were removed from the biological cycle when covered with water or soil, undergoing anaerobic degradation and ultimately becoming part of the sediments. The most concentrated forms of these sediments became the fossil resources used today for energy and raw material applications. As an endothermic reaction, photosynthesis represents a process that converts radiative energy into chemical energy that connects an energy flow (solar radiation) and a material reaction flow (reducing carbon in its oxidized form into reduced forms in organic molecules).
5. Conversion rates of materials and energy in present industrialized societies have reached high values. These are – in the prominent example case of fossil carbon, but also for other materials – significant for the natural global system of material reservoirs and exchange flows, e.g. for the relatively small atmospheric carbon reservoir, into which fossil CO_2 emissions are released.
6. The recent example of chlorofluorocarbons (CFC) emissions – contributing to the greenhouse effect and causing the Antarctic ozone hole – has shown that successful global political action is possible. The widespread adaption of the Montreal Protocol on Substances Depleting the Ozone Layer will lead to a responsible usage of chlorinated substances in the future. Thus one can expect that the ozone hole will cease in a few decades.
7. As a general orientation, human societies should make optimum use of and integrate in natural energy flows and material cycles. There are large amounts of solar energy available – although with low flux densities – that can be converted into heat and electricity. This flow is constantly present and can be used for manifold human activities. In addition, driven by photosynthesis, there are huge flows of biological carbon fixation, which store energy in chemical form. This chemical energy is dissipated once the living organisms die. It is a technical challenge to make optimum use of this high-energy biomass. However, biomass cultivation for energy application should be limited by land use changes that would affect the global carbon system and decrease the overall photosynthesis productivity on Earth to a significant degree.
8. Industrialized countries should use their large wealth in technical knowledge and experience in order to develop sustainable technologies. These will contribute to better development perspectives for less-developed countries. However, with their present conversion rates of material and energy, they cannot serve as an example for less-developed countries. Limitations in available natural resources and global environmental effects require serious actions towards a convergence of material and energy conversion rates of industrialized and less-developed countries. This is in the interest of both sides.
9. Technology options in order to be suitable for future development, should include as high priorities:

  a) supply of low-temperature heat based on solar radiation (solar collectors), ambient thermal energy, or on combined processes (cogeneration of electricity and heat), thus replacing combustion in this application,
  b) vehicles for individual mobility with high energy efficiency (e.g. recovery of braking energy, low weight),
  c) renewable electricity as an energy source for vehicles (especially low-weight), high-density fuels for aviation synthesized from renewable resources with improved technologies that are to be developed,
  d) energy-use of biomass based on efficient and clean upgrading processes (e.g. to liquid fuels), integrated in other kinds of biomass utilization (for food, feed, chemicals),
  e) electricity generation based on a variety of renewable technologies, fluctuation/intermittence of solar and wind-based power generation compensated by electrical network management and efficient storage technologies, assisted by fossil fuel technologies for a limited transition time, preferably with reliable carbon capture and sequestration,
  f) for increased utilization of solar energy flows in the future, technology options should combine large-scale and smaller-scale approaches.

10. Climate engineering (geoengineering) methods to counteract the warming effects of anthropogenic greenhouse gas emissions appear to be less attractive. The efficiency of these technologies on a global scale has not yet been demonstrated and obvious risks and conflicts (e.g. with food production) exist. In the face of limited available resources, priority should be given to the development of sustainable technologies.
11. Process engineers may contribute their systematic approach in the formulation of material and energy balances for dynamic systems. They are used to working with mathematical models of mass and energy transfer rates, kinetics of chemical and biological transformations, and understand dynamic systems behavior (stability, multiple solutions, etc.). Among their tasks is the quantitative treatment of complex reaction kinetics as they may represent source or sink terms in material balance equations for individual species in the biogeosphere.
12. Ambitious political actions should be enforced as defined in Germany after the Fukushima incident in 2011, to initiate and support the transformation of national energy systems. This transformation should primarily address significant reductions of fossil CO_2 emissions and efficiency increases in energy conversion and utilization. Further negotiations must lead to international agreements, defining national development strategies, individual contributions based on national aspects such as cumulated CO_2 emissions in the past, economic capacities, forest resources, etc. Successful programs implemented in the past (e.g. Montreal Protocol on Substances Depleting the Ozone Layer, *man to the moon* project, or local/regional environmental protection programs) should be remembered and serve as inspiration. Avoiding drastic climate changes will contribute to decrease the risk of large-scale migration and significant international conflicts.

13. In addition to technology development and political actions, individual consumer behavior and changes in prosperity criteria must contribute to a decrease in non-renewable energy and material flows. Non-material, cultural, and social activities should help human individuals to develop creativity in various fields, making optimum use of, for example, new media and information technologies. Today's prosperous societies are challenged to develop and demonstrate lifestyles with low energy and material consumption. Progress in technology development alone will not be sufficient for sustainable development, even with the highest energy and material efficiencies.

Appendix

Decimal Multipliers as Unit Prefixes

zetta	Z	10^{21}
exa	E	10^{18}
peta	P	10^{15}
tera	T	10^{12}
giga	G	10^{9}
mega	M	10^{6}
kilo	k	10^{3}
hecto	h	10^{2}
deca	da	10^{1}
deci	d	10^{-1}
centi	c	10^{-2}
milli	m	10^{-3}
micro	μ	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}
femto	f	10^{-15}
atto	a	10^{-18}

Common Energy Units and Conversion Factors

	J	kWh	kg OE[a]	kg CE[b]	eV	cal
1 J =	1	2.78×10^{-7}	2.3×10^{-8}	3.42×10^{-8}	6.25×10^{18}	0.239
1 kWh =	3.6×10^{6}	1	0.86×10^{-1}	0.12	2.25×10^{25}	8.6×10^{5}
1 kg OE[a] =	4.18×10^{7}	11.63	1	1.43	2.63×10^{26}	1.0×10^{7}
1 kg CE[b] =	2.93×10^{7}	8.14	0.7	1	1.84×10^{26}	7.0×10^{6}
1 eV =	1.6×10^{-19}	4.43×10^{-26}	3.81×10^{-27}	5.44×10^{-27}	1	3.81×10^{-20}
1 cal =	4.18	1.16×10^{-6}	1.0×10^{-7}	1.43×10^{-7}	2.61×10^{19}	1

[a] Oil (petroleum) equivalent, historical definition: 10 000 kcal kg^{-1}

[b] Coal (hard coal) equivalent, historical definition: 7000 kcal kg^{-1}

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Glossary

Some of the following definitions were adapted, with modifications, from the IPCC Fourth Assessment Report, Working Group I Report, The Physical Science Basis, Annex I.

Aerosol Airborne solid or liquid particles, with a typical size between 0.01 and 10 μm, that reside in the atmosphere for at least several hours. Aerosols may be of either natural or anthropogenic origin. Aerosols may influence climate in several ways: (i) directly through scattering and absorbing radiation, and (ii) indirectly by acting as cloud condensation nuclei or modifying the optical properties and lifetime of clouds.

Albedo The fraction of solar radiation reflected by a surface or an object. Snow-covered surfaces have a high albedo, the surface albedo of soils ranges from high to low, and vegetation-covered surfaces and oceans have a low albedo. The average albedo of the Earth amounts to about 0.3.

Anthropogenic emissions Emissions of greenhouse gases, greenhouse-gas precursors, and aerosols associated with human activities. These include the burning of fossil fuels, deforestation, land-use changes, livestock, fertilization, etc. that result in a net increase in emissions.

Atmosphere The gaseous layer surrounding the Earth. The dry atmosphere consists mostly of nitrogen (77.7 % volume mixing ratio), oxygen (20.9 %), and argon (0.93 %) together with a number of trace gases, such as neon, helium and radiatively active greenhouse gases such as carbon dioxide (0.04 %) and ozone. In addition, the atmosphere contains the greenhouse gas water vapor, whose amounts are highly variable with an average global volume mixing ratio of 0.4 %. The atmosphere also contains clouds and aerosols.

Base load generator Technical installation to generate electricity in (relatively) constant operation, in order to supply electricity to the distribution grid on a base-load level.

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Biodiversity Biological diversity characterizes the variety of animal and plant species in a region, in an ecosystem and in the biogeosphere as a whole. Studies of biodiversity include the variety and complexity of biological species and effects of human activities on natural changes.

Bioenergy Energy derived from biomass.

Biogeosphere System or entirety of processes in and interrelations between the biosphere and the inanimate environment, in the region of the Earth extending from the atmosphere to the maximum depth at which organic life exists.

Biomass The total mass of living organisms, usually expressed as dry weight. Organic matter consisting of, or recently derived from, living organisms (especially regarded as fuel) excluding peat.

Biomes Biomes are major regional elements of the biosphere. They are characterized by typical communities of plants and animals, representing several ecosystems (e.g. forests, rivers, ponds, and swamps within a region).

Biorefinery Technical installation including a variety of chemical or biotechnological processes, in order to convert biomass raw materials into a collection of intermediate products for chemical syntheses (e.g. commodity chemicals), end products, and/or fuels. This is analogous to petroleum refineries.

Biosphere The entirety of all living organisms on Earth.

Bitumen High-viscosity crude hydrocarbon mixtures, that are a member of the petroleum family. Bitumen can be upgraded to high-quality fuels, in analogy to conventional oil refining, however with higher energy demand.

Black body Material that completely absorbs all irradiation arriving at its surface, resulting in zero reflection (or albedo).

Carbon capture and storage (CCS) Strategy and technology for capturing CO_2 emissions from fossil fuel combustion (e.g. by means of scrubbing processes), in order to store the captured CO_2 in suitable spaces underground (or in the ocean). This strategy could be called a secondary-measure-strategy, i.e. the pollutant is formed and afterwards removed. In contrast, primary-measure-strategies would avoid formation of the pollutant.

Carbon dioxide A naturally occurring gas, which is also a by-product of burning fossil fuels from fossil carbon deposits, such as oil, gas and coal, of burning biomass, and of land use changes and other industrial processes. Carbon dioxide is starting material for photosynthesis. It is one of the most important greenhouse gases that affects the Earth's radiative balance. It is the reference gas against which all other greenhouse gases are measured and therefore has a global warming potential of 1.

Carbon intensity Characteristic value for correlating fossil carbon flow (with resulting CO_2 emissions) in a national economy and gross national income (GNI). It is a measure for the dependence of a national economy on fossil fuel input.

Carbon-free electricity Electricity generated without using a (fossil) carbon-based fuel.

Catalyst A chemical substance, used in small amounts relative to the reacting components, that modifies (usually increases) the rate of a reaction without being consumed in the process.

Chemical energy Energy stored in materials, which can be released in a chemical reaction (e.g. combustion with air) and converted into other forms of energy. Chemical energy generally has favorable characteristics regarding energy density (per volume, per mass), which is important for energy storage or mobile applications.

Chemical reactor A container where chemical reactions are carried out, often equipped with installations for mixing and heat transfer.

Chlorofluorocarbons (CFCs) Greenhouse gases covered under the 1987 Montreal Protocol and used for refrigeration, air conditioning, and other purposes. Since they are not destroyed in the lower atmosphere, CFCs are able to reach the upper atmosphere where they participate in catalytic destruction of ozone.

Climate Climate is defined as the average weather, or more rigorously, as the statistical description in terms of the mean and variability of relevant quantities over a period of time ranging from months to thousands or millions of years. The classical period for averaging these variables is 30 years. The relevant quantities are most often surface variables such as temperature, precipitation, and wind.

Climate engineering Technological efforts to stabilize the climate system by direct intervention in the energy balance of the Earth for reducing global warming.

CO_2 equivalent Amount or concentration of CO_2 that causes the same change in radiative forcing as a given mixture of CO_2 and other greenhouse gases.

CO_2 intensity See carbon intensity.

Coal Carbon-based solid fuel, formed predominantly from higher plants under anaerobic conditions (i.e. covered by layers of ground or ocean, separated from the atmosphere).

Coal equivalent Amount of energy stored in a mass unit of standard coal (1 kg coal equivalent contains 29.4 MJ, that can be released as heat during combustion).

Coal liquefaction Chemical conversion of solid coal to liquid fuels, to be used e.g. for transport applications. Liquefaction can be done either directly, by adding hydrogen, or indirectly, via gasification to synthesis gas (CO and H_2) as an intermediate.

Cogeneration plant Technical installation for converting primary energy into electricity and heat for utilization, in order to overcome the limited efficiency of thermal electricity generation processes.

Commodity chemicals Chemicals produced in the chemical industry, to be used for chemical syntheses for a wide variety of final products, also called bulk chemicals, which are produced in large quantities.

Cryosphere The component of the Earth system consisting of all snow, ice and frozen ground (including permafrost) on and beneath the surface of the Earth and ocean.

Designer fuel Chemical fuel produced in the chemical upgrading of raw materials, which are tailored to the specific requirements of the application process (e.g. synthetic hydrocarbons for combustion in an internal combustion engine).

District heating Technical installation for heat generation in quantities suited for large building complexes or residential districts. The quantities of heat to be generated allow for simultaneous generation of electricity at acceptable cost, and thus for achieving high overall efficiencies.

Dobson Unit (DU) A unit to measure the total amount of ozone in a vertical column above the Earth's surface. The number of Dobson units is the thickness in units of 10^{-5} m that the ozone column would occupy if compressed into a layer of uniform density at a pressure of 1.013 hPa and a temperature of 0 °C. A typical value for the amount of ozone in a column of the Earth's atmosphere is 300 Dobson Units.

Earth system The entirety of Earth's spheres and their complex interactions.

Ecosystem A system of living organisms interacting with each other and their physical environment. The boundaries of an ecosystem depend on the focus of interest. The extent of an ecosystem may range from very small spatial scales to the entire planet Earth.

Efficiency The ratio of energy output and energy input for an energy conversion process.

Energiewende Terminology in German for a strategy to convert a complete national energy system from the fossil (and nuclear) primary source basis, as it has developed historically. Fossil and nuclear energy sources are to be replaced to a very large (or complete) extent by renewable energy sources (solar, wind, biomass, geothermal, hydro, and ocean energy). Energiewende (transition of energy system) implies innovations in technology, infrastructures, institutions and consumer behaviour, supported by political actions. Aim is to avoid serious damage to the global climate.

Energy The amount of work or heat delivered. Energy is classified in a variety of types and becomes useful to humans when it flows from one place to another or is converted from one type into another. Primary energy is the energy embodied in natural resources (e.g. coal, crude oil, natural gas, uranium) that has not undergone any anthropogenic conversion. It is transformed into secondary energy by cleaning (natural gas), refining (oil in oil products), or by conversion into electricity or heat. When the secondary energy is delivered at the end-use facilities it is called end energy (e.g. electricity at the wall outlet), where it becomes usable energy (e.g. light).

Energy balance The energy budget of a control volume or system. If this balance is positive, warming occurs; if it is negative, cooling occurs. Averaged over the globe and over long time periods, this balance must be zero as the amount of incoming solar radiation on average must be equal to the sum of the outgoing reflected solar radiation and the outgoing thermal infrared radiation emitted. A perturbation of this global radiation balance, be it anthropogenic or natural, is called radiative forcing.

Energy storage Energy storage receives new attention in the context of solar and wind power generation. With their fluctuating and intermittent generation characteristics, storage is important for matching disparities between supply and demand. Electricity can then be stored as such or after conversion in the form of gravitational, thermal, pressure-volume energy, or as chemical fuel energy.

Estimated ultimate recovery (EUR) Estimated amounts of raw material (e.g. petroleum, metal ores), present before anthropogenic utilization began.

Evapotranspiration The combined process of evaporation from the Earth's surface and transpiration from vegetation.

Exergy The maximum amount of useful (mechanical or electrical) work that can be obtained from matter in contact with its environment. The exergy of most fossil fuels is very similar to their higher heating value (HHV).

Feedback An interaction mechanism between processes is a feedback when the result of an initial process triggers changes in secondary processes that in turn influence the initial one. A positive feedback intensifies the initial process, while a negative feedback reduces the initial process.

Ferrel cell An indirect, atmospheric flow pattern in the mid-latitudes driven by the direct Hadley cells.

Fischer–Tropsch synthesis A chemical process for the conversion of synthesis gas, a mixture of CO and H_2 which can be obtained from different carbon sources such as biomass (renewable), natural gas (most widely used today), and coal (the first source historically and also used today), to hydrocarbons. Fischer–Tropsch synthesis was developed in the early 20th century in Germany and is now utilized worldwide for the production of synthetic fuels.

Flow A quantity per unit time exchanged over the boundary of a system. Earth receives a permanent flow of radiative energy from the Sun. Another example is the mass flow of carbon dioxide emitted to the Earth's atmosphere through burning of fossil fuels.

Fluidized bed gasification Chemical conversion of a solid or liquid raw material into gaseous products, e.g. synthesis gas ($CO + H_2$), fuel gas, or substitute natural gas.

Flux density A flow per unit surface area. On average, Earth receives a flux density of $341\,\mathrm{Wm}^{-2}$ radiative energy from the Sun.

Fossil CO_2 emissions Emissions of CO_2 resulting from the combustion of fossil fuels, i.e. petroleum, coal and gas. In the context of the global carbon cycle, these emissions transfer carbon stored in fossil deposits into the atmosphere, with the potential of increasing the carbon reservoir in the atmosphere.

Fossil fuel Carbon-based fuel from fossil organic deposits, including coal, peat, petroleum, and natural gas, which is formed in anaerobic chemical and biological decomposition reactions from biomass that was separated from the atmosphere. Fossil fuels release thermal energy (or heat) when they are oxidized with oxygen.

Fuel (chemical or nuclear) Material that can be used for energy generation, either by chemical reactions (combustion) or by nuclear reactions (fission, fusion).

Fuel cell A technical energy conversion process which converts chemical energy (stored in a chemical fuel) directly into electricity. It is also suited for small-scale applications.

Global climate model (GCM) A numerical representation of the climate system based on the physical, chemical and biological properties of its components, their interactions and feedback processes, and accounting for all or some of its known properties. Global climate models coupling atmosphere, ocean, and ice provide a comprehensive representation of the climate system.

Global warming The gradual increase, observed or projected, in global surface temperature, as one of the consequences of radiative forcing caused by anthropogenic emissions.

Global warming potential An index, based upon radiative properties of well-mixed greenhouse gases, measuring the radiative forcing of a unit mass of a given greenhouse gas in the present-day atmosphere integrated over a chosen time horizon (usually 100 a), relative to that of carbon dioxide.

Greenhouse effect Greenhouse gases effectively absorb infrared radiation emitted by the Earth's surface. Atmospheric radiation is emitted to all sides, including downward to the Earth's surface. Thus, greenhouse gases trap heat within the surface–atmosphere system. Infrared radiation emitted to space at the top of the atmosphere being in balance with the incoming radiation from the Sun corresponds to an average temperature of $-18\,^\circ\mathrm{C}$ whereas the Earth's surface is kept at a much higher temperature of, on average, $+15\,^\circ\mathrm{C}$.

Greenhouse gas Gaseous constituents of the atmosphere, both natural and anthropogenic, that absorb and emit radiation at specific wavelengths within the spectrum of infrared radiation emitted by the Earth's surface, the atmosphere, and clouds. Water vapor (H_2O), carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), and ozone (O_3) are the primary greenhouse gases. Moreover, there are a number of entirely human-made greenhouse gases in the atmosphere, such as the halocarbons and other chlorine- and bromine-containing substances, dealt with under the Montreal Protocol.

Gross national income (GNI) Total sum of economic values of all products and services in a national economy.

Gross primary production (GPP) The amount of biomass produced via photosynthesis per square area and per time (dry organic matter), equivalent to the amount of radiative energy converted, without loss due to respiration of the growing plants.

Haber–Bosch process An industrial process for the manufacture of ammonia from hydrogen and nitrogen developed in the early 20th century. Ammonia is required for nitrogen fertilizers and essential for food production for the growing World Population.

Hadley cell A direct, thermally driven overturning cell in the atmosphere consisting of a poleward flow in the upper troposphere, subsiding air into the subtropical anticyclones, return flow as part of the trade winds near the surface, and rising air near the equator.

Heating value Chemical energy content of a chemical fuel, that can be released as heat during combustion. The *higher* heating value (*HHV*) is obtained if liquid water is the reaction product, while the *lower* heating value (*LHV*) corresponds to the formation of gaseous water.

Heavy crude oil Petroleum with high viscosity and low hydrogen-to-carbon ratio. Chemical upgrading (refining) to high-value liquid fuels is more difficult than in the case of standard petroleum.

Hydrosphere The component of the Earth system comprising liquid surface and subterranean water, such as ocean, seas, rivers, fresh water lakes, underground water, etc.

Insolation The amount of solar radiation reaching the Earth. Usually insolation refers to the radiation arriving at the top of the atmosphere. Sometimes it is specified as referring to the radiation arriving at the Earth's surface.

Internal combustion engine (Otto or Diesel) Technical device for converting chemical energy (stored in a chemical fuel) into power via combustion.

Kyoto Protocol The Kyoto Protocol was adopted in 1997 in Kyoto and contains legally binding commitments to reduce anthropogenic greenhouse gas emissions (carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride) by at least 5 % below 1990 levels during the commitment period 2008–2012.

Latent heat The amount of heat transported from the Earth's surface to the atmosphere that is associated with evaporation or condensation of water vapor at the surface.

Liquid hydrocarbons (Diesel, gasoline or petrol) Liquid fuel, most commonly used for transport applications, in combustion engines of cars and ships, or gas turbines of airplanes. They have high energy densities and are presently produced via petroleum refining.

Liquid petroleum gas (LPG) Product from petroleum refining that contains C_3- and C_4-hydrocarbons with boiling points near ambient conditions. They can easily be liquefied at ambient temperature by applying elevated pressure and re-gasified for utilization by reducing the pressure.

Lithosphere The solid outer layer of the Earth, including the crust and the upper part of the mantle.

Luminosity The amount of energy emitted by a star, or other astronomical objects, per unit time. Sun has a total power output of 3.846×10^{26} W or 341 W m^{-2} related to Earth's surface.

Material cycle System of reservoirs in which a material is distributed in different forms (chemical species, gaseous, liquid, and solid), interacting by exchange flows (chemical or biological reactions, phase changes, i.e. evaporation, condensation, melting, solidification).

Microalgae Eukaryotic, one- or multi-cellular organisms such as bacteria, vira, archaea, etc. They are active in photosynthesis, live in aquatic ecosystems, and contribute large amounts of biomass to global net primary production. High productivity values are achieved, because microalgae, due to their aquatic environment do not need (ligno)cellulosic materials, but can reinvest in productive structures. They are currently investigated as a source for food, chemicals, or fuel production.

Microgasturbine Technical device for converting chemical energy (of a chemical fuel) into electricity and heat. It is a small-scale application of the gas turbines used in airplanes or in electric power plants.

Mitigation strategy Strategy for human activities to reduce the sources or enhance the sinks of greenhouse gases.

Montreal Protocol The Montreal Protocol on Substances that Deplete the Ozone Layer was adopted in Montreal in 1987, and subsequently adjusted and amended in London (1990), Copenhagen (1992), Vienna (1995), Montreal (1997) and Beijing (1999). It controls the consumption and production of chlorine- and bromine-containing chemicals that destroy stratospheric ozone, such as chlorofluorocarbons, methyl chloroform, carbon tetrachloride, and others.

Milankovich cycles Variations in eccentricity, axial tilt, and precession of the Earth's orbit around the Sun that determine climatic conditions on Earth.

Natural gas Carbon-based gaseous fuel, containing mainly methane, formed during formation reactions of either petroleum or coal at anaerobic conditions.

Net primary production (*NPP*) The amount of biomass produced via photosynthesis per square area and per time (dry organic matter). *NPP* is equivalent to gross primary production decreased by the loss due to respiration of the plant.

Nonlinear process A process is called nonlinear when there is no simple proportional relation between cause and effect. The climate system contains many such nonlinear processes, resulting in a system with a potentially very complex behavior. Such complexity may lead to abrupt climate change.

Oil equivalent Amount of energy stored in a mass unit of standard petroleum (1 kg oil equivalent contains 41.87 MJ, released during combustion).

Ozone Ozone, the triatomic form of oxygen (O_3), is a gaseous atmospheric constituent. In the troposphere, it is created both naturally and by photochemical reactions involving gases resulting from human activities (smog). Tropospheric ozone acts as a greenhouse gas. In the stratosphere, it is created by the interaction between solar ultraviolet radiation and molecular oxygen (O_2). Stratospheric ozone plays a dominant role in the stratospheric radiative balance and is an efficient shield for ultraviolet solar radiation.

Ozone layer Stratospheric layer in which the concentration of ozone is the greatest extending from about 12 to 40 km above the Earth's surface. Every year, during the Southern Hemisphere spring, a very strong depletion of the ozone layer (ozone hole) takes place over the Antarctic region, caused by anthropogenic chlorine and bromine compounds in combination with the specific meteorological conditions of that region. See also Montreal Protocol.

Peak oil Moment in the history of anthropogenic petroleum utilization, when maximum production rates are achieved. It is generally assumed that peak oil will not be far in the future, given the decrease in high-quality petroleum reserves that are easy to access and to refine.

Peaking plant Technical installation for generation of electricity to supply electricity demand peaks, operating on demand.

Petroleum Carbon-based liquid fuel formed predominantly from marine biomass under anaerobic conditions.

Petroleum coke Solid by-product of petroleum refining, rich in carbon.

Photon flux density (*PPFD*) Energy flow values of radiation per square area, often defined to be equivalent to photosynthetic photon flux density, and sometimes expressed as the flow of photons per square area.

Photosynthesis The process in organisms by which carbohydrates are synthesized from carbon dioxide and water using light as an energy source. Oxygen is released as a byproduct in most forms of photosynthesis.

Phytomass The amount of living biomass present per square area in different biomes, representing the reservoir of biomass (and of organic carbon) per square area.

Primary energy Energy raw materials, solar irradiation or derived forms (wind, hydro, ocean, etc.), which can be converted into energy carriers for end use (fuels, electricity).

Radiative forcing The change in the net vertical irradiance (expressed in Wm^{-2}) at the tropopause due to an internal change or a change in the external forcing of the climate system, such as, for example, a change in the concentration of CO_2 or in the output of the Sun.

Reaction enthalpy Energy (or enthalpy) change connected to a chemical reaction, as change per amount of reactant converted.

Reserves Amount of a raw material available for anthropogenic utilization, which is known in quantity and recoverable under present economic conditions.

Reservoir A component of the Earth system which has the capacity to store, accumulate, or release a substance of concern, e.g. carbon.

Residence time Characteristic time describing how long a component or part of a flow remains in a system.

Resources Amount of a raw material for anthropogenic utilization including estimated (not known) quantities and also recoverable under potential future economic conditions.

Respiration The process whereby living organisms convert organic matter to carbon dioxide, releasing energy and consuming molecular oxygen.

Solar heat collector Technical device for converting solar irradiation into low-temperature heat, to be used for heating of buildings and other applications.

Stratosphere Region of the atmosphere above the troposphere extending from about 10 km to about 50 km altitude.

Sustainability Goal of development for human societies that meets the needs of the present generation without compromising future generations. The concept of sustainability aims at an integrated approach to economic, social, and environmental processes.

Synfuels (synthetic fuels) Chemical fuels generated in technical chemical conversion processes, starting with fossil or biomass raw materials (e.g. synthetic liquid hydrocarbons, methane, hydrogen).

System A set of interacting or interdependent elements that form an integrated whole. A system is confined by a system boundary and enclosed in an environment. A *closed* system, such as the Earth, is in contact with the environment (space) through exchange of energy, but does not exchange matter. An *open* system, such as Earth's atmosphere, may exchange both energy and matter.

Tar sand Mixture of sand grains, water, and a high-viscosity crude hydrocarbon mixture called bitumen. Bitumen is a member of the petroleum family.

Thermodynamics The science of energy conversions. The first law of thermodynamics states that the sum of all energies is constant. According to the second law, there are energy forms with different quality. Energy conversions are always accompanied by quality losses.

Troposphere The lowest part of the atmosphere, from the surface to about 10 km in altitude at mid-latitudes, where clouds and weather phenomena occur. In the troposphere, temperatures generally decrease with height.

Weathering Physical or chemical processes leading to erosion of Earth's rocks, soils, and minerals under the influence of the atmosphere.

List of Symbols

Constants

c	speed of light $= 2.998 \times 10^{8}\,\mathrm{m\,s^{-1}}$	Eq. (3.1)
g	acceleration of gravity $= 9.80665\,\mathrm{m\,s^{-2}}$	Eq. (2.2)
h	Plank's constant $= 6.6262 \times 10^{-34}\,\mathrm{J\,s}$	Eq. (3.1)
k	Boltzmann's constant $= 1.3806 \times 10^{23}\,\mathrm{J\,K^{-1}}$	Eq. (3.1)
R	ideal gas constant $= 8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}}$	Eq. (1.7)
σ	Stefan–Boltzmann constant $= 5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$	Eq. (3.3)

Dimensionless Numbers

St	Stanton number	Eq. (1.12)

Greek Letters

η	efficiency		Eq. (1.18)
ε	emitted power per unit area and wavelength	$\mathrm{W\,m^{-2}\,m^{-1}}$	Eq. (3.1)
γ	climate sensitivity	$\mathrm{K\,m^{2}\,W^{-1}}$	Eq. (3.11)
λ	wavelength of radiation	m	Eq. (3.1)
μ	specific growth rate	different	Eq. (3.16)
ν_i	stoichiometric coefficient of component i		
ρ	molar density	$\mathrm{mol\,m^{-3}}$	Eq. (1.8)
τ	residence time	s	Eq. (4.1)

Latin Letters

A	area	$\mathrm{m^{2}}$	
a	albedo		Eq. (3.4)

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b	birth rate	s^{-1}	
c_i	molar concentration of component i	$mol\,m^{-3}$	
c_p	molar heat capacity	$J\,mol^{-1}\,K^{-1}$	
d	death rate	s^{-1}	
E_A	activation energy	$J\,mol^{-1}$	Eq. (1.7)
E	exergy	$J\,mol^{-1}$	Eq. (1.20)
F	flow	different	
H	enthalpy	J or $J\,mol^{-1}$	
J	flux density	different	
K	capacity		Eq. (2.8)
k	rate constant	s^{-1}	
k_0	frequency factor	s^{-1}	
M	molar mass	$kg\,mol^{-1}$	
m	mass	kg	
N	number of species		
n	amount of substance	mol	
P	precipitation	$mm\,a^{-1}$	Eq. (3.14)
p	pressure	mol	Eq. (2.2)
Q	heat	J	
q	heat transfer parameter	K^4	Eq. (3.25)
r	rate	different	
RF	radiative forcing	$W\,m^{-2}$	Eq. (3.11)
S	entropy	$J\,K^{-1}$	Eq. (1.19)
T	temperature	K	
t	time	s	
V	volume	m^3	
W	work	J	
X	conversion		Eq. (1.19)
y	interaction parameter	different	
z	altitude	m	Eq. (2.2)

Subscripts

abs	absorbed
ad	adiabatic
a	atmosphere
av	average
B	black
el	electric
em	electric
F	fertile
f	formation
H	hare
horiz	horizontal

L	lynx
mech	mechanical
m	mass
n	amount of substance
rad	radiative
R	reaction
rev	reversible
s	surface
util	utilized
W	white

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