

## Chapter 2

# Climate and Carbon Cycle

### 2.1 Climate: Definition and Prerequisites

Climate, as defined by IPCC (2001, 2007), is the “average weather” at a given period of time and space. In a more statistical understanding, this period of time, ranging in various reports from months to thousands of years, was eventually adopted by the World Meteorological Organization (WMO) to be 30 years.

Temperature, precipitation, and wind are the most commonly used quantities to describe climate and to classify it into specific categories assigned to different parts of the world. There are three basic systems used to categorize weather: (1) Thornthwaite’s system, based on the precipitation-to-vapour ratio varying for different areas, (2) system based on air masses identification as the main component forming climate system, (3) Köppen’s system (Peel et al. 2007; Martyn 2000; Kalkstein et al. 1996). The latter is most widely applied to describe the world’s climate, based on average monthly values of temperature and precipitation; their yearly patterns allowed to differentiate between the five basic climate types:

Type A (tropical)—occurring in the equatorial zone, characterized by continuously high temperatures (monthly averages above 18°C) and abundant, year-round, precipitation;

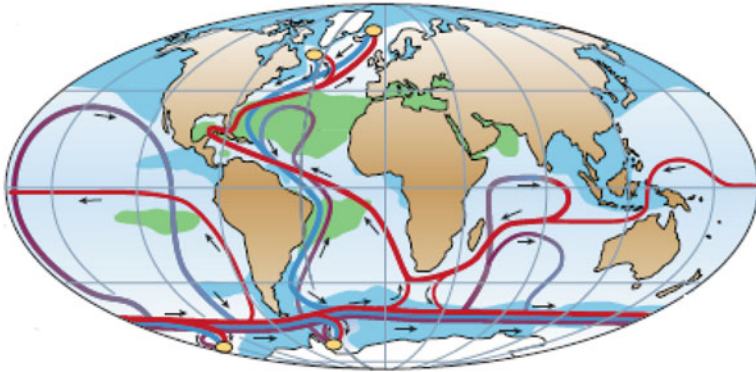
Type B (dry)—distinctive for vast areas of North Africa, the Arabian Peninsula and Australia, characterized by scarce precipitation and large temperature amplitudes.

Type C (moderate)—characterized by mild winters, occurring in the mid-latitude regions (e.g., Western Europe)

Type D (continental)—mid-latitude zone climate characterized by cool winters (average temperatures of the warmest and the coolest month oscillate above and below 10°C, respectively),

Type E (polar)—typical for high latitude regions, characterized by cool summers (average temperature of the warmest month below 10°C) and cold winters.





**Fig. 2.2** Scheme of the thermohaline circulation (Rahmstorf 2002)

Earth's axis and transformations in the shape of the Earth's orbit, lasting approximately 23, 41, 100 thousand years, respectively.

The differences in a landscape is what determines climate at regional and local scales, varying with height above the sea level, as well as with the distance of the land from the major water bodies that make the transfer between seasons smoother. Both of the above aspects, combined with latitude radiation changes, are causing climate variability that depends on the location (Martyn 2000).

Another important factor controlling climate at the local and regional scales is the relationship between high and low atmospheric pressure systems (Martyn 2000). North Atlantic, for example, is dominated by the Icelandic Low and the Azores High, which decides about the air masses circulation over Europe. Positioning and intensity of both pressure systems change over years, and combined with accompanying events is called North Atlantic Oscillation (NAO; Hurrell 1995). NAO explains about 30 percent of the ocean winter temperatures dynamics north of 20°N (Greatbatch 2000). Similarly, El Niño-Southern Oscillation (ENSO) describes atmospheric circulation over the Pacific Ocean equatorial zone (McPhaden et al. 2006). The range of ENSO repercussions reach vast areas globe wide (Rosenzweig 1994).

Both circulation patterns are directly related to ocean currents pattern (thermohaline circulation)—the World Ocean water circulation process, based on deepwater formation at high latitude regions, mostly in the North Atlantic and around the Antarctica (Fig. 2.2; Rahmstorf 2003). Thus, together with warm surface currents, large amounts of heat are transported to the Arctic region. During the process of gradual water cooling the heat is transferred to the atmosphere (Trenberth and Caron 2001).

The results of a climate model presented by Stocker (2002), that does not involve occurrence of the thermohaline circulation, demonstrated that in this scenario the Southern Hemisphere would cool down insignificantly, whereas the temperature for the Northern Hemisphere, especially in the North Atlantic region, would decrease by several degrees Centigrade. Disruptions of the circulation could

have been a possible cause of rapid climate changes during the last glaciations (Ganopolski and Rahmstorf 2001; Rahmstorf 2002).

Aerosols—droplets and particles reflecting the solar radiation and limiting its amount that reaches the surface, are another essential factor influencing the Earth's climate (Charlson et al. 1992). Aerosols, as the condensation nuclei in the course of clouds formation, contribute to the increase of albedo (Twomey 1974; Roberts et al. 2008). However, due to the multiplicity and complexity of the aerosols interactions, the estimates of climate transformations range due to the aerosols are still charged with a significant error (IPCC 2001, 2007). Among natural constituents of aerosols, those playing a key role are: sea salt, dust from the dry regions (e.g., Sahara), organic substances of marine and terrestrial origin, and sulfur compounds (originating, mainly, from sea water and volcanic eruptions; Andreae 2007). Paleoclimatic reconstructions indicate the volcanic eruptions as the main cause of the climate transformations in the Earth's past (Robock 2000; Gao et al. 2008).

Climate is also determined by the atmosphere composition. To this end the greenhouse gases play the most significant role (IPCC 2001, 2007). About 30 percent of solar radiation reaching the atmosphere is reflected back into the outer space. The remaining 70 percent heats the lower atmosphere and the planetary surface. In order to balance the heat that reaches the Earth, the planetary surface emits infrared radiation (IR) back into the outer space. Part of the IR is absorbed by the greenhouse gases causing the atmosphere temperature increase—the mechanism called a greenhouse effect (Kiehl and Trenberth 1997).

This phenomenon allows to maintain the Earth's temperature at a level that is both high enough and stable to create habitable conditions on the Earth surface. Among the most important greenhouse gases are: water vapour, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO and CFCs. Due to its partial pressure and the absorption spectrum, water vapour plays the key role in the atmosphere, contributing up to 95 percent of the greenhouse effect (Le Treut et al. 2007), while the role of the remaining gases is, at least, one order of magnitude smaller. Nonetheless, paleoclimate studies clearly indicate that global temperature variations are largely related to CO<sub>2</sub> and CH<sub>4</sub> concentrations changes. This conclusion is based on the both gases concentrations in the ice core collected in the Antarctic (Lake Vostok). The deepest layers of the core are dated on 400,000 years BP (Petit et al. 1999), allowing to reconstruct climate of the several glaciations (Monnin et al. 2001). Moreover, as demonstrated by Clark and Mix (2000), significant change in CO<sub>2</sub> concentration was accompanying glacier retreat about 19,000 years ago, strengthening the effect caused by the Sun radiation increase.

### ***2.1.2 Climate Change and Anthropogenic Influences***

During the last few decades there has been increasing interest in the range and intensity of anthropogenic activities influencing the environment. Worldwide impact of socio-economic development resulting in the climate alteration has been

the main concern of the major scientific projects, e.g., JGOFS (Karl et al. 2001), IGBP (IGAC 2006), CARBOEUROPE, and CARBOOCEAN (Schulze et al. 2009), as well as a reason for the political concern (e.g., IPCC 2007).

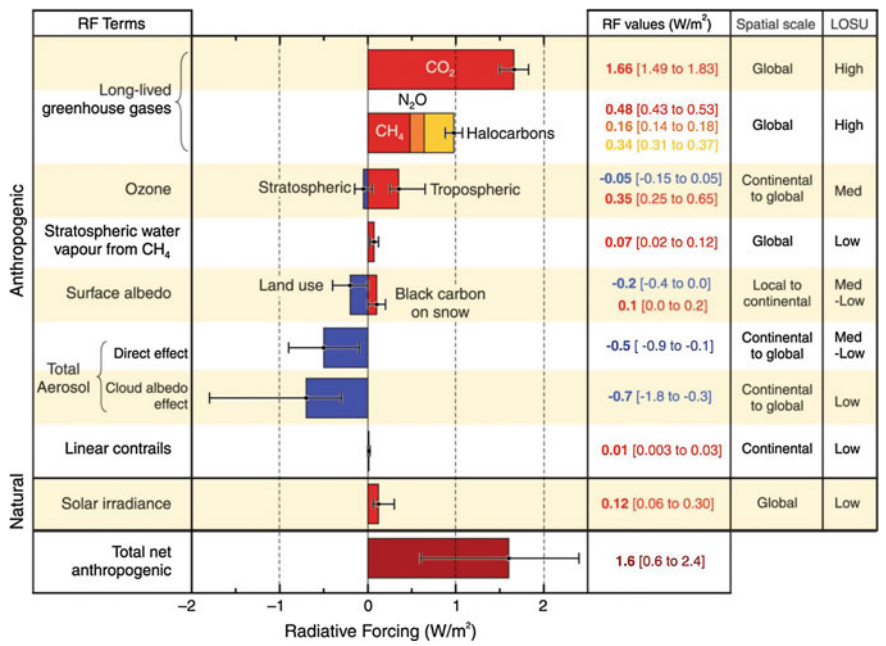
The prerequisite for the initiation of climate change is a shift in the Earth's energy balance that may be a consequence of at least one of the following mechanisms (Le Treut et al. 2007):

- Change in the amount of solar radiation reaching the Earth's surface—mechanism independent of anthropogenic activity, as described in Sect. 2.1.1.
- Change in the ratio of incident to reflected solar radiation (albedo)—mechanism depending on both anthropogenic activity and naturally occurring events in the environment.
- Change in the IR radiant flux being re-emitted by the surface—mechanism depending on anthropogenic factors (greenhouse gases concentration in the atmosphere).

The surface covered by ice (cryosphere) has a great impact on the Earth's albedo (Groisman et al. 1994). For example, solar radiation is much more efficiently reflected from a surface of ice, characterized by albedo of 0.8, than from other regions of the Earth, with albedo averaging at around 0.3.

The low average albedo of the Earth's surface is determined primarily by a large surface area and low albedo ( $<0.1$ ) of the ocean (Le Treut et al. 2007). Recent studies demonstrate that the cryosphere surface has been reduced in size with simultaneous weight loss of the ice, estimated at 7,000 Gt (Gt =  $10^9$  tons) in the period 1960–2003. Clark et al. (1999) demonstrated that snow and ice melting rates are significantly enhanced by positive feedback from the albedo decrease. An additional factor lowering the cryosphere's albedo, particularly in the Northern Hemisphere region, is caused by the increasing amount of soot particles. Among the important sources of these airborne contaminants are the fossil fuel and biomass burning (Hansen and Nazarenko 2004; Jacobson 2004). On the other hand, the Earth's albedo is enhanced by aerosols produced by humans, mainly in combustion processes (Fig. 2.3; Penner et al. 2001, 2003, 2004). A common criterion used to differentiate between aerosols is their chemical composition (Forster et al. 2007):

- Sulphate aerosols—originating mostly from fossil fuels combustion processes (72%), while biomass combustion contributes merely 2% of the total. The other important aerosols are: dimethyl sulfide (DMS) produced by phytoplankton, amounting to 19% of the total; and sulphites formed during volcanic activity, amounting to 7% of the total (Penner et al. 2001).
- Organic aerosols—formed during combustion processes of fossil fuel, biofuels, and burning of forest areas. Ito and Penner (2005) estimated that about 2.2 Tg (Tg =  $10^{12}$  g) of particulate organic matter (POM) is emitted annually from fossil fuels combustion and 7.5 Tg from biofuels combustion. The present-day rates for organic aerosols emission are three orders of magnitude higher than in 1870.



**Fig. 2.3** Global radiation forcing for specific constituents in 2005, in relation to the year 1750, together with levels of scientific understanding (LOSU; IPCC 2007)

- Nitrate aerosols—their formation depends on substantial concentrations of ammonia and nitric oxide in the atmosphere. The nitrate aerosols are of lesser significance than sulphate aerosols (Schaap et al. 2004).
- Mineral dust—derived from naturally occurring processes (e.g., Sahara); 30–50% of the dust originates from human activity such as agriculture, cement production and melioration (Tegen and Fung 1995). Estimates regarding mineral dust contribution in the energy balance are contradictory (Forster et al. 2007).
- Carbon soot—unlike the aerosols described above, it is characterized by a positive radiation forcing.

The overall effect of aerosols originating from the anthropogenic activity on the Earth’s albedo is additionally strengthened by changes occurring on the land (Fig. 2.3). Deforestation, forests burning and arable areas expansion are main processes contributing to the changes (Forster et al. 2007). Increase in the Earth’s albedo caused by development in agriculture is, on the other hand, especially pronounced in mid-latitude regions, where during the winter period meadows and arable areas are coved by snow more expansively than forest areas. Klein Goldewijk (2001) suggest that the actual meadow and arable areas expanded from 7.9–9.2 mln km<sup>2</sup> (6–7% of the total land area) in 1750 to 45.7–51.3 mln km<sup>2</sup> (35–39%) in 1990, with simultaneous decrease in total forest areas by 11 mln km<sup>2</sup>.

However, the estimate of the effects of the above transformations and their influence on the Earth's albedo is still charged with a considerable error (Fig. 2.3; IPCC 2007; Forster et al. 2007).

In contrast to aerosols, characterized by the greatest negative radiation forcing, the greenhouse gases are a key element leading to an increase in global temperatures (Fig. 2.3; IPCC 2007). The impact of anthropogenic greenhouse gases began around 8,000 years ago (Ruddiman 2005). Starting from then the natural variability of CO<sub>2</sub> concentration in the atmosphere has no longer correlated with Milankovitch cycles (natural changes in the Earth's surface insolation; Bates 1987). Assumed cause of this change, that occurred 8,000 years ago, is the beginning of agricultural settlements in the Northern Hemisphere. Deforestation had been leading to increased CO<sub>2</sub> emission to the atmosphere, decreasing at the same time the natural absorptive capacity of the biosphere in relation to CO<sub>2</sub> (Ruddiman 2003). In the case of CH<sub>4</sub>, a similar divergence dates back to about 5,000 years ago, related to extensive agricultural practices, mainly rice production in South-East Asia (Ruddiman 2003).

According to IPCC (2007) report, the major greenhouse gases entering the atmosphere which result from human activity include: CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and freons (Fig. 2.3). In particular, concentration of freons increased significantly during the 1990s, as a result of widespread use of freons in refrigerators, cosmetics production and pressurized polymers (Velders et al. 2005). Although the freon and related compounds concentrations in the atmosphere are relatively small (approx. 10<sup>6</sup> times lower than CO<sub>2</sub>), their high capacity to absorb the infrared radiation contributes significantly to the greenhouse effect (Fig. 2.3; Forster et al. 2007).

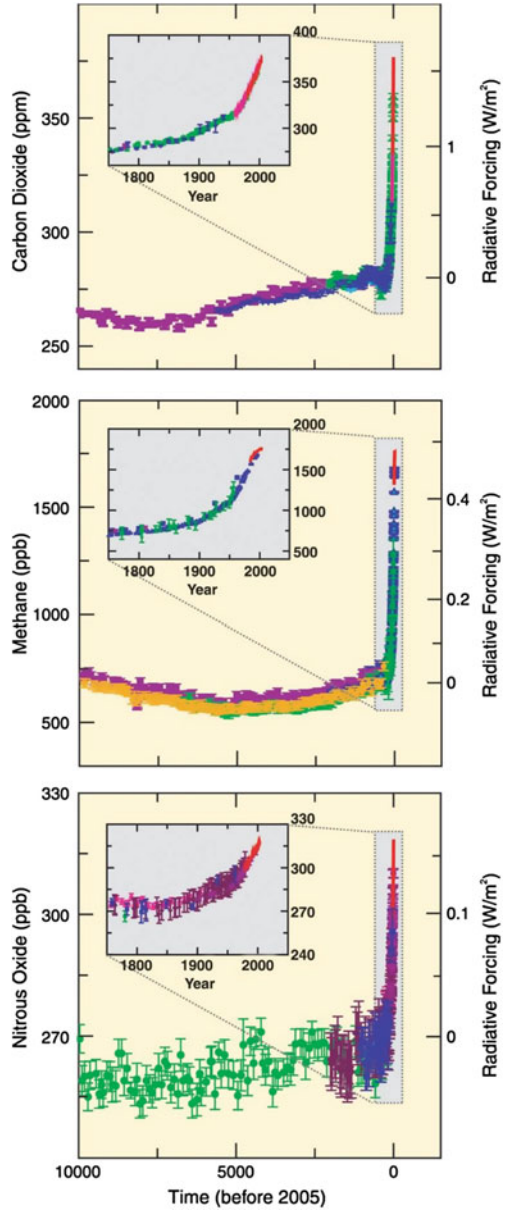
The relative increase in concentration of methane (CH<sub>4</sub>) in the atmosphere began in 1750 (Fig. 2.4; Forster et al. 2007). This greenhouse gas is characterized by the highest after CO<sub>2</sub> radiation forcing. The most important anthropogenic sources of CH<sub>4</sub> in the atmosphere include agriculture, especially rice cultivation, cattle breeding, landfills and leaks in systems extracting and transporting natural gas (Forster et al. 2007).

Regular monitoring of methane concentrations in the atmosphere indicates significantly reduced growth rate and stabilization of methane during recent years (Dlugokencky et al. 2003). However, the mechanisms of these changes are not fully understood (Forster et al. 2007).

Among all the greenhouse gases, CO<sub>2</sub>, that most significantly contributes to an increase in the global temperature, deserves a special attention (IPCC 2007). Radiative forcing of CO<sub>2</sub> in 2005 compared to 1750 exceeds the sum of radiative forcing of all the remaining greenhouse gases (Fig. 2.3). In addition to the natural sources of CO<sub>2</sub> in the atmosphere, that are associated mainly with the organic matter cycle, human introduces even more CO<sub>2</sub>, which further disrupts the environmental balance, leading to the climate warming. The main sources of the anthropogenic CO<sub>2</sub> include: the fossil fuels combustion (Forster et al. 2007), cement production (Worrell et al. 2001), deforestation—especially tropical forests (Houghton 2003; Strassmann et al. 2008), and—to a smaller extent—the biomass combustion (Andreae and Merlet 2001).

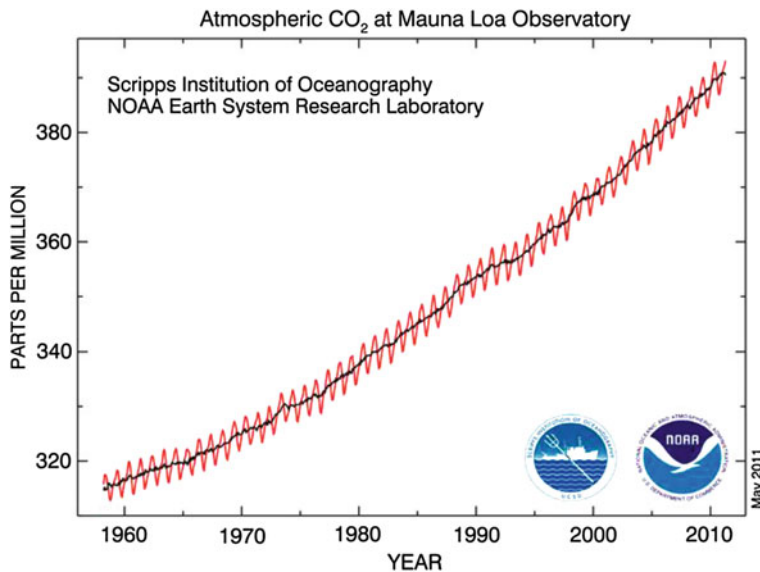


**Fig. 2.4** Concentrations of atmospheric  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  during the last 10,000 years, reconstructed from ice cores. Different colors indicate different sources of data. Results of recent measurements are in red. Radiative forcing is calculated in relation to the year 1750 (IPCC 2007)



Intensification of these processes, especially in recent decades, in particular the fossil fuels combustion, has led to a significant increase in the atmospheric  $\text{CO}_2$  concentration (Fig. 2.5; Keeling et al. 1995). The monitoring studies initiated in the late 1950s (Fig. 2.5) suggest large seasonal variations of  $\text{CO}_2$  in the atmosphere, caused by heterogeneous emission of anthropogenic  $\text{CO}_2$  during the year,





**Fig. 2.5** Changes of the atmospheric CO<sub>2</sub> over decades; observatory Mauna Loa, Hawaii (source: <http://www.esrl.noaa.gov>)

as well as significant contribution of naturally occurring processes contributing to the global carbon cycle. Therefore, research that leads to understanding of the mechanisms controlling CO<sub>2</sub> concentration in the atmosphere should be in the center of today's earth sciences interests. Uncertainty regarding the magnitude of anthropogenic CO<sub>2</sub> emission in the future, due to the socio-political and economic interactions of a modern world, gives a further motivation to take actions (IPCC 2007).

### 2.1.3 Global Consequences of the Climate Change

It is assumed, with a high certainty, that human activity, primarily the greenhouse gases emission, has led to a global temperature increase (IPCC 2007). It is also believed, although with limited certainty, that these actions prevented a new ice age to begin from 3,000 to 4,000 years ago (Ruddiman 2003; Ruddiman et al. 2005). According to the last IPCC report (IPCC 2007), the measurable increase of the global temperature during the last fifty years is a direct evidence of human interference with the atmosphere composition. Models that are taking into account only natural radiative forcing indicated clearly the inevitability of cooling for this period of time. Studies conducted by Trenberth et al. (2007) show that the average global temperature for the period from 1906 to 2005 increased by  $0.74 \pm 0.18^{\circ}\text{C}$ , while the temperature increase during the last fifty years has been two times faster

than during the entire century and amounted to  $0.013^{\circ}\text{C year}^{-1}$ . This value is relatively small, mainly due to the heat exchange through vast ocean surface, which moderates the temperature changes. Above the continents, the temperature has been rising since 1979 at a rate of  $0.027^{\circ}\text{C year}^{-1}$ . Furthermore, the temperature increase varies in different parts of the world, and in some regions (Arctic and Antarctic) is subject to large fluctuations during subsequent decades (IPCC 2007; Trenberth et al. 2007).

Rapid, from the viewpoint of geological time scale, temperature increase carries numerous consequences, which not only disturb the environment as a whole and its compartments, but also force changes in mankind development. One of the major effects of the atmospheric temperature rise is melting of mountain glaciers, ice sheets and a decrease of both the sea ice surface and volume (IPCC 2007). This is due to impaired annual balance of ice growth and diminishing. High rates of this phenomenon allow to track the process of an ice regression over time—as short as one generation span (Georges 2004; Klein and Kincaid 2006; Gordon et al. 2008). Drinking water resources shrinkage is one of the immediate results of melting glaciers. Approximately 1/6 of the globe population live within or near river basins supplied by water fed from melting glaciers and periodically occurring snow (Kundzewicz et al. 2007). Diminishing glaciers have also their socio-economical aspect due to employment rate of the local communities, often relying on tourism and winter sports (Breiling and Charamza 1999). At a global scale, melting of glaciers influences the air masses circulation, as demonstrated by changes taking place in the Himalaya Mountains (Lemke et al. 2007), and, to some extent, sea level (IPCC 2007).

The cryosphere melting is a direct cause of rising sea level (Hagen et al. 2003; Alley et al. 2005). It is estimated that in the period from 1961 to 2004 the water from melting glaciers has been increasing the sea level in a rate of  $0.5 \pm 0.18 \text{ mm year}^{-1}$ . During recent years this process has become even more pronounced, and the rate of melting, expressed as the raising sea level, increased to  $0.77 \pm 0.22 \text{ mm year}^{-1}$  (Lemke et al. 2007). In the case of ice sheets, diagram of long term trends is less precise, because their volume is subjected to large fluctuations over decades (IPCC 2007). However, recent studies (Lemke et al. 2007) indicate that the melting ice sheet of Greenland contributed from 0.14 to  $0.28 \text{ mm year}^{-1}$  to a rate of sea level increase, during the period 1993–2003. Estimates for Antarctica are less precise and oscillate, for the same period of time, between  $0.55 \text{ mm year}^{-1}$  (increase in sea level) and  $-0.14 \text{ mm year}^{-1}$  (decrease).

The total contribution of cryosphere to a global sea level increase for the years 1993–2003 is estimated at  $1.2 \pm 0.4 \text{ mm year}^{-1}$  (Lemke et al. 2007). The risk carried by the melting ice is stressed by the fact that the water volume stored in the ice sheet of Greenland and Antarctica, expressed as an equivalent of sea level rise, amounts to about 64 m (Lythe et al. 2001; Lemke et al. 2007). However, no one expects that the sea level rise will exceed 1–2 m by the end of this century.

Thermal expansion of water also influences the sea level (Miller and Douglas 2004). Bindoff et al. (2007) estimate that in the period 1961–2003 the global average temperature of the oceans increased by  $0.1^{\circ}\text{C}$ . This contributed to the sea

level increase at a rate of  $0.4 \pm 0.1 \text{ mm year}^{-1}$ . Similarly to the rate of melting glaciers, the influence of water thermal expansion on the sea level increase has intensified over the past several decades. The value for the period from 1993 to 2003 has been estimated to be  $1.6 \pm 0.5 \text{ mm year}^{-1}$ . When summed up with the cryosphere melting it gives the sea level increase rate of  $2.8 \pm 0.7 \text{ mm year}^{-1}$  (IPCC 2007).

Results of paleoclimatic reconstructions suggest a natural oscillation of the sea level reaching as much as 120 m (Fairbanks 1989). However, during the last 3,000 years or more, the sea level was stable. When the recent trends continue, a risk of local, and regional, flooding of low-lying areas will materialize in the nearest future (Bindoff et al. 2007; Nicholls et al. 2007).

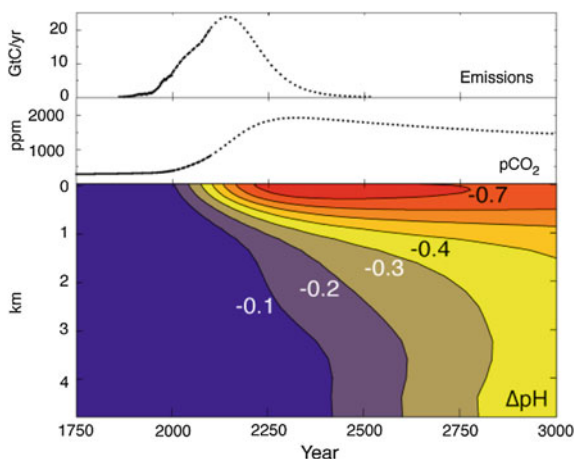
Another consequence of elevated concentration of  $\text{CO}_2$  in the atmosphere, related directly to the oceans, is sea water acidification (Fig. 2.6; Caldeira and Wickett 2003; IPCC 2007). The sea water pH is determined primarily by the so-called carbonate buffering system—the presence of ions and, simultaneously, of dissolved  $\text{CO}_2$ . The increase of  $\text{CO}_2$  in the atmosphere results in the increase of partial pressures difference of the gas between the atmosphere and the ocean. This, in turn, leads to the diffusion of  $\text{CO}_2$  into water (mechanism described in some detail in Sect. 2.2.3.2). In this way, the present day carbonate equilibrium is disturbed resulting in pH lowering. This is a particular threat for the marine organisms that built their shells out of  $\text{CaCO}_3$ , whose stability depends directly on the pH of water (Feely et al. 2004; Orr et al. 2005). The gradual drop of the seawater pH has amounted to 0.1 pH unit (Fig. 2.6). Direct measurements indicate that the rate of pH drop increased in the last twenty years to 0.02 pH units per decade (Bindoff et al. 2007).

The climatic changes bring also an increasing number of extreme events (Kundzewicz et al. 2004; Trenberth et al. 2007) recognized as ‘low frequency of occurrence events’. These are often characterized by high intensity, and pronounced effects, e.g., erosion, material losses, storms and storm surges (BACC Author Team 2008). Trenberth et al. (2007) indicate at the increase in intensity and frequency of occurrence of tropical cyclones, hurricanes, typhoons, being related directly to an increase of the surface water temperature in tropical regions.

An increase of the average global precipitation was also observed during the 20<sup>th</sup> century. At the same time, the frequency of intense rainfalls has increased (Trenberth et al. 2007), resulting in numerous flooding events (Ulbrich et al. 2003) and droughts, particularly since the 1970s (New et al. 1999; Kundzewicz 2009). Extremely dry weather conditions are more often encountered in tropical and sub-tropical, as well as mid-latitude regions, e.g., Western Europe. Droughts occur, commonly, along with the unusually high temperatures (Trenberth et al. 2007).

Global material losses attributed to extreme events increased eight times during the last 40 years (inflation included). Proportion of goods insured against the natural disasters has also increased over the recent years. This situation is related partly to the growing wealth and development of societies, but also largely to the growing frequency of the extreme climate events occurrence (Mills 2005; Beniston 2007; Kundzewicz 2009).

**Fig. 2.6** Predicted pH changes in the ocean, based on target values of CO<sub>2</sub> emission and concentration in the atmosphere (Caldeira and Wickett 2003). The *Y* axis represents alternately the extend of CO<sub>2</sub> emission to the atmosphere (*topmost* dependence), concentration of CO<sub>2</sub> in the atmosphere (*middle*) and the pH drop through the depth of the ocean



Climate changes exert pressure on the natural ecosystems. According to Fischlin et al. (2007), approximately 20–30% of flora and fauna species will be endangered before 2100. This is a consequence of rising temperature and the atmospheric CO<sub>2</sub> concentration to levels unrepresented during the last 650,000 years for CO<sub>2</sub>, and 740,000 years for temperature (Fischlin et al. 2007). Negative changes will also affect marine ecosystems, mostly organisms built of CaCO<sub>3</sub>, coral reefs being particularly threatened (Riebesell et al. 2007; Wei et al. 2009). The projected increase in thermal stratification for the tropical and mid-latitude ocean zones can lead to reduction of primary production in these regions (Doney 2006).

The transformations that are observed now and projected for the future, and their consequences, provoke the society to act against these perturbations or, at least, to adapt to them. Challenges, that the future generations will be facing include:

- Providing food and drinking water to a constantly growing population, affected by more frequent and intense climate events and shifts of climatic zones (Easterling et al. 2007; Bański 2009);
- Development of systems that warn and protect population against the extreme climate events (Kundzewicz 2009);
- Evoking public awareness about the existing risks and adaptation means (Kundzewicz 2009);
- Protection of the public health against harmful effects of the climate warming (Confalonieri et al. 2007; Błażejczyk 2009);
- Protection of the endangered areas, primarily coastal and polar regions (Nicholls et al. 2007; Anisimov et al. 2007);
- Deepening of the knowledge about mechanisms determining the magnitude of anthropogenic factors influencing the Earth's climate, particularly concerning the global carbon cycle (IGBP 2002; IPCC 2007; Gutry-Korycka 2009; Schulze et al. 2009).

Assuming more conscious human actions and accepting the responsibility for climate changes, preventing transformations becomes crucial, especially in the field of greenhouse gases reduction in the atmosphere (IPCC 2007). This is possible to achieve by optimizing energy generating technologies and developing alternative energy sources (IPCC 2007; Kintisch 2009).

All the above actions involve considerable costs, that very often exceed a single country budget, in particular budgets of developing countries. Thus there is a need for balanced responsibility, shared between the developed and developing countries (IPCC 2007; Kintisch 2009).

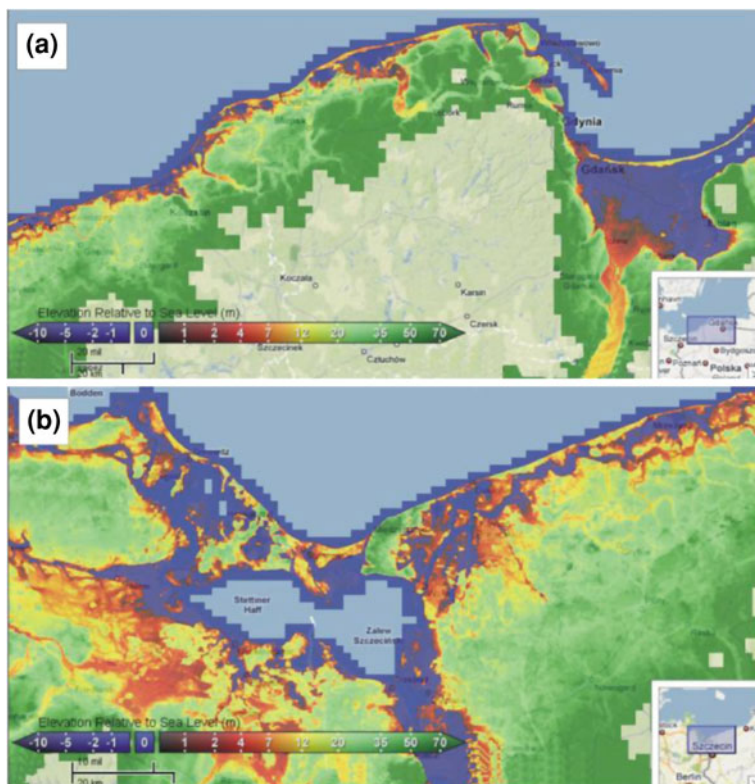
### ***2.1.4 Climate Change Consequences in the Baltic Sea Region***

The Baltic Sea climate is characterized by a large seasonal variability, typical of its geographical location, topography of the catchment area, and the sea–land interactions (HELCOM 2007). Characterized by western winds dominance, the south-western part of the basin is under a strong influence of the North Atlantic and the Gulf Stream. This effect weakens in the north-eastern direction, where the continental influences and polar air masses dominate. Winter season climate features, for the Baltic, and most of the Europe are determined mainly by NAO (BACC Author Team 2008).

Many of the conditions determining changes within the Baltic Sea region are identical to those that control other parts of the world (BACC Author Team 2008). Against a background of globally increasing temperature, estimated for the period 1861–2000 to raise by  $0.05^{\circ}\text{C decade}^{-1}$ , the warming of the Baltic Sea region seems to be actually greater, reaching up to  $0.08^{\circ}\text{C decade}^{-1}$  (HELCOM 2007).

Sea level is quite dynamic in the Baltic. An important factor contributing to the Baltic basin bathymetry is related to isostatic movements of the Earth's crust. It is estimated that, as a result of these movements, the bottom of the Gulf of Bothnia uplifts at a rate of 10 mm per year, whilst the southern part of the Baltic Sea lowers by 0.5–2 mm per year (Wyrzykowski 1985; Harff et al. 2001; Johansson et al. 2004). Changes occurring in the North Sea and the North Atlantic also impact sea level in the Baltic (Pempkowiak et al. 2009). Models suggest that, by the year 2100, the Baltic Sea level will rise in the range from 46 (Danish Straits) to 100 cm (Polish coastal zone), with simultaneous drop from several to several dozen centimetres in the Gulf of Bothnia (Fenger et al. 2001; Miętus et al. 2004; Schmidt-Thomé et al. 2006; Pempkowiak et al. 2009). Such a high increase of the water level poses a threat, especially to low-lying areas, with Polish coast being particularly exposed. Pempkowiak et al. (2009) estimate that as much as  $1,800\text{ km}^2$  of the area along the sea shore could be covered with water (Fig. 2.7). According to Schmidt-Thomé et al. (2006), significant losses could be also observed in the City of Gdansk and within the Vistula Delta.

The effect of rising water levels in the Baltic is enhanced by storms and storm surges (Pempkowiak et al. 2009) and by predictably more frequent occurrence of



**Fig. 2.7** Map of the Southern Baltic coast, threatened by inundation as a result of rising sea level: **a** central and eastern coast; **b** Pomeranian Bay and the Szczecin Lagoon coasts. Colours correspond to the elevation of coastal areas (source: [www.globalwarmingart.com](http://www.globalwarmingart.com))

extremely intensive rainfalls in this part of Europe (HELCOM 2007). These factors pose a considerable threat to the regions situated in vicinity of estuaries; an example may be the unexpected flood that struck Gdańsk, a port city on the southern Baltic coast, in 2001 (Majewski 2003). Storm occurrence frequency is expected to increase during the coming decades, while trends in wave height are not demonstrated (Miętus 1999; Meier et al. 2004; Schmidt-Thomé et al. 2006). Rising sea level, as well as storm events and storm surges escalation, can lead to an enhanced erosion of sea shores. Redeposition coefficient—shore line regeneration to its erosion ratio—is an often used measure to describe erosion intensity. The data compiled by BACC Author Team (2008) suggest that the value of the coefficient for the Polish coastline has been decreasing: for the period 1875–1979 the redeposition coefficient amounted to 69%, between 1960 and 1983 it was reduced to 20%, to reach just 14% during 1971–1983. The combination of the above-mentioned factors creates a risk for the local infrastructure: residential areas, agricultural holdings, tourist resorts, and ports (Liszewska 2004; Pempkowiak et al. 2009).



Climate transformations carry important consequences for the Baltic Sea ecosystem (HELCOM 2007; BACC Author Team 2008). The atmosphere temperature increase leads to reduction of convective mixing, followed by nutrients cycles alterations and anoxic conditions in the water layers below the halocline. Anoxia and hypoxia are of particular importance in the reproductive cycle of cod. Changes in the population of this top Baltic predator result in transformations along the entire food chain (Mackenzie et al. 2007). Temperature increase transforms also the ecosystem structure, by favouring the warm water species over the cold water ones (e.g., cyanobacteria vs. diatoms; Wasmund and Uhlig 2003). Impact of the projected decrease in salinity and water acidification (Stigebrandt and Gustafsson 2003), caused by elevated CO<sub>2</sub> concentration (Omstedt et al. 2009) will additionally accelerate the Baltic Sea ecosystem transformations (HELCOM 2007).

## 2.2 Global Carbon Cycle

### 2.2.1 Carbon Reservoirs

Carbon belongs to the most widespread chemical elements on Earth, yet constitutes only  $0.0012\% \pm 0.00036\%$  of its total mass (Lécuyer et al. 2000). There are three carbon isotopes occurring in nature: two stable isotopes, <sup>12</sup>C and <sup>13</sup>C, and radioactive <sup>14</sup>C (half-life about 5,730 years; Sulzman 2007). Despite its low contribution to the earth mass, carbon is fundamental for life on Earth, being the essential element present in all known life forms. Another story, but of great significance, is the previously described greenhouse effect determined, to a great proportion, by carbon compounds.

Data concerning reservoirs and carbon fluxes among the environment compartments have been cataloged and published in numerous recent studies (e.g., Doney et al. 2003; Sarmiento and Gruber 2006; Houghton 2007; Emerson and Hedges 2008; Schulze et al. 2009). The majority of available reports are based on the same source data, and present comparable estimates, with differences seldom exceeding few percent. For the purpose of the present summary, the compilations of data by Emerson and Hedges (2008) and by IPCC (2007) have been used (see Fig. 2.8).

Carbon is present in all the three domains of the natural environment: land, water and atmosphere. The smallest amount of carbon, mainly in the form of CO<sub>2</sub>, is present in the atmosphere. It is estimated that the amount of atmospheric carbon dioxide, during the pre-industrial period, was approximately 612 Pg (Pg = 10<sup>15</sup> g), compared to the current 784 Pg. A comparable amount, of roughly 600 Pg, is typically assigned to terrestrial organisms, with dominating proportion (80%) of carbon occurring in the plants biomass. Additional 1,500 Pg of carbon is gathered in soil. Another reservoir of carbon are the fossil fuels in the Earth's crust, which are currently the most widely used sources of energy. The greatest



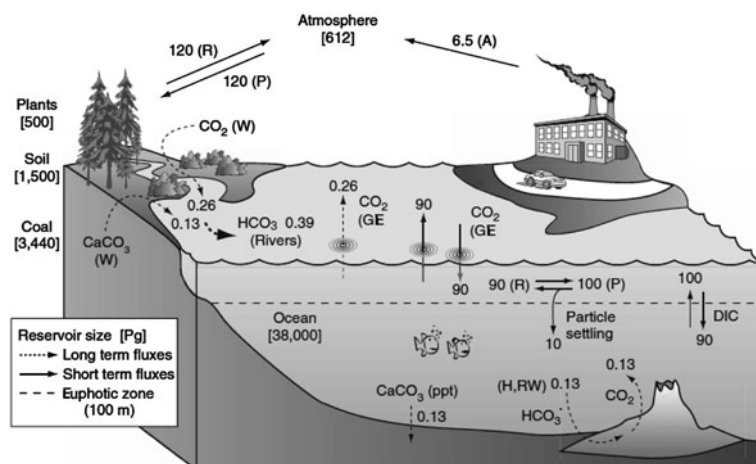
carbon amount occurs in rocks: coal, lignite, slate and oil shale. It is estimated that these minerals contain up to a total of 3,440 Pg of carbon. Much less carbon is present in oil deposits (about 90 Pg) and natural gas (about 44 Pg). However, the dominant reservoir of carbon is the ocean. The amount of carbon accumulated there is equal to 38,000 Pg, which represents 80% of the total carbon mass in the Earth crust. Furthermore, 1,000 Pg of carbon is deposited in marine sediments. Contribution of marine organisms is less significant (Fig. 2.8; Emerson and Hedges 2008).

### ***2.2.2 Scheme of the Global Carbon Cycle in the Environment***

The carbon cycle is a part of the global matter cycle. The amount of carbon comprised in individual reservoirs (Sect. 2.2.1) illustrates their potential impact on the cycle. The principal matter carrier in the carbon cycle is  $\text{CO}_2$ . In the absence of human influence, carbon cycle is characterized by the steady state (Fig. 2.8). Carbon exchange between individual reservoirs involves four fundamental processes: photosynthesis, respiration, gas exchange through the water/atmosphere interface and weathering.

Photosynthesis and respiration are the primary processes facilitating carbon exchange between the land and the atmosphere. During the photosynthesis, organisms capable of carbon assimilation, mostly plants and cyanobacteria, absorb  $\text{CO}_2$ , and, with participation of  $\text{H}_2\text{O}$  and solar energy, they synthesize organic compounds forming the organisms' biomass. Animals and microorganisms, as the successive levels of a food chain, utilize the biomass, enabling further carbon cycling. Most of the living organisms oxidize organic matter in order to generate energy necessary for them to function. Besides energy,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are the final products of the oxidation. The resulting  $\text{CO}_2$  is most often released to the atmosphere. Carbon dioxide exchange between land and the atmosphere is estimated at  $120 \text{ Pg C year}^{-1}$  (assuming complete respiration of organic matter on land, without including erosion and, resulting from erosion, dissolved carbon species runoff to the ocean; Fig. 2.8; Emerson and Hedges 2008). In a global scale, erosion (approximately  $0.4 \text{ Pg year}^{-1}$ ) does not play a significant role (Schulze et al. 2009). Somewhat smaller amounts of carbon are subject to the exchange through the water/atmosphere interface, estimated at  $90 \text{ Pg C year}^{-1}$  (Fig. 2.8; Emerson and Hedges 2008). Processes of absorption/emission of  $\text{CO}_2$  by seas and oceans, and carbon fluxes in the marine environment are described, in some details, in Sects. 2.2.3 and 2.2.4.

Weathering involves physical and chemical processes. The latter, named chemical weathering, is caused by the atmospheric  $\text{CO}_2$ , that, combined with  $\text{H}_2\text{O}$ , reacts with carbonate and silicate rocks. The result of weathering are ions, which, together with river water, are discharged to the ocean. It is estimated that two-thirds of this load is represented by ions derived from carbonates, mostly  $\text{CaCO}_3$ , and the remaining one-third from silicates, weathering. The contribution of



**Fig. 2.8** Scheme of the global carbon cycle (Emerson and Hedges 2008). Data expressed in Pg [ $10^{15}$  g]. Carbon resources for individual components are marked by *square brackets*. *Dashed arrows* indicate long-term fluxes, *solid arrows*—short term fluxes. Symbols: W weathering, GE gas exchange through the water/atmosphere interface, P photosynthesis, R respiration (oxidation), H hydrothermal processes, RW rock weathering

weathering processes to the global carbon fluxes is negligible, since the total carbon flux related to weathering amounts to, roughly,  $0.39 \text{ Pg C year}^{-1}$  (Emerson and Hedges 2008).

The steady state global carbon cycle had been disturbed by human activity (Sect. 2.1.2). According to the 4<sup>th</sup> IPCC report (IPCC 2007), the anthropogenic  $\text{CO}_2$  emission to the atmosphere has been increasing yearly. In 2004 it was estimated at  $10.4 \text{ Pg C year}^{-1}$ , being remarkably higher (by 80%) than the emission recorded in 1970. This represents more than 8% of the natural  $\text{CO}_2$  exchange between land and sea, and over 11% of exchange between the ocean and the atmosphere (Emerson and Hedges 2008). Estimated that, in the period from 1800 to 1994, nearly  $244 \text{ Pg C}$  reached the atmosphere as a result of anthropogenic activity. This is close to twice the amount of known carbon resources stored as crude oil and natural gas, however less than 10% of carbon reserves deposited as coal (Sect. 2.2.1).

Still, the existing fossil fuel deposits, and possible scenarios of the socio-economic development, suggest that by 2030 the emission of anthropogenic  $\text{CO}_2$  to the atmosphere can amount to between 140% and 210% of the current levels. Thus, the anthropogenic contribution is likely to be comparable to the natural processes determining  $\text{CO}_2$  fluxes in the environment (IPCC 2007).

Quantitative assessment of the anthropogenic  $\text{CO}_2$  releases refers to the gas emission during the 1990s (IPCC 2001, 2007). The data demonstrate that as a result of combined fossil fuels combustion and cement production,  $6.3 \pm 0.4 \text{ Pg C year}^{-1}$  reached the atmosphere, out of which close to  $3.2 \pm 0.1 \text{ Pg C year}^{-1}$  (50%) had

been retained in the atmosphere. The remaining  $3.1 \text{ Pg C year}^{-1}$  had been absorbed by the land plants ( $1.4 \pm 0.7 \text{ Pg C year}^{-1}$ ) and oceans ( $1.7 \pm 0.5 \text{ Pg C year}^{-1}$ ; Sabine et al. 2004; Emerson and Hedges 2008). The smaller contribution of the continents (despite greater natural  $\text{CO}_2$  exchange with the atmosphere compared to the ocean; Fig. 2.8.) is explained by the shrinkage of intensive photosynthesis areas, mainly tropical forests (Sect. 2.1.2). The shorter time of carbon residence on land than that in the ocean, also plays a significant role (Schulze et al. 2009). Estimates by other authors (Quay 2002; Takahashi et al. 2002; Canadell et al. 2007; Houghton 2007) of the anthropogenic  $\text{CO}_2$  fluxes in the environment are close to these described above, while differences between the individual estimates fall within the error limits.

### ***2.2.3 Carbon Cycle in the Marine Environment***

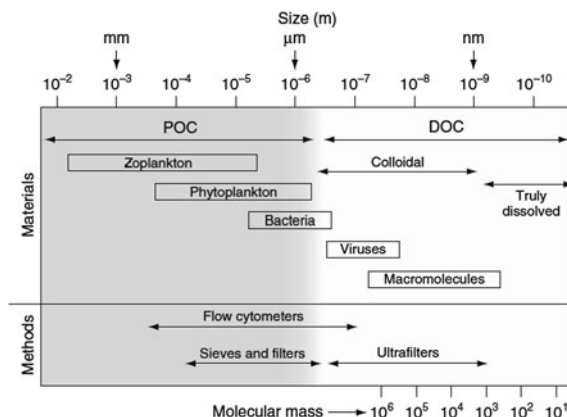
Significant accumulation of carbon loads in the ocean (Sect. 2.2.1) and the ocean significant contribution to the anthropogenic  $\text{CO}_2$  absorption (Takahashi et al. 2002) intensified studies that led to advances in the marine environment carbon cycle, especially during the last decade (Sarmiento et al. 1998; Stein and Macdonald 2004; Sarmiento and Gruber 2006; Emerson and Hedges 2008). In order to access the role of the seas and oceans in the global carbon cycle, complex biogeochemical models are designed that are supposed to reflect mathematically the processes occurring in marine systems (Maier-Reimer and Hasselmann 1987; Siegenthaler and Joos 1992; Doney et al. 2003; Sasai and Ikeda 2003; Watson and Orr 2003; IPCC 2007). The models are largely based on the experimental studies conducted during cruises of research vessels, and data collected using semi-automated instruments installed on different types of buoys, platforms and commercial vessels (Bates et al. 2000; Sayles and Eck 2009).

#### **2.2.3.1 Carbon Concentration and Forms in Seas and Oceans**

Carbon in the marine environment occurs in a variety of forms, from ions characterized by a small molecular weight to large particles suspended in water column. Filtration is the method commonly used to separate the suspended fraction from the dissolved carbon. In the oceanographical studies, the most commonly used are glass fiber filters and cellulose membranes with the pore size ranging from  $0.2$  to  $1 \text{ }\mu\text{m}$ , while the commonly adopted boundary between dissolved and particulate species is  $0.45 \text{ }\mu\text{m}$ . This allows for separation of zooplankton, phytoplankton, majority of bacteria and detritus as particulate matter. The filtrate comprises: viruses, colloids, and dissolved substances (Fig. 2.9; Hedges 2002; Emerson and Hedges 2008).

The criterion used to differentiate carbon species in seawater is the division into organic and inorganic carbon fractions. These in turn are divided according to their

**Fig. 2.9** Size of carbon containing components of seawater and methods used to separate and differentiate between the components (Emerson and Hedges 2008)



properties, origin and function in the environment. There are four basic forms of carbon in seawater:

- Dissolved inorganic carbon (DIC).
- Particulate inorganic carbon (PIC).
- Dissolved organic carbon (DOC).
- Particulate organic carbon (POC).

In the marine environment, DIC, as the most abundant carbon species, plays the dominant role in the carbon cycle. Moreover, estimated at 98% of the total carbon that occurs in water, DIC represents the largest resource of carbon globally (Emerson and Hedges 2008). In surface waters, DIC concentrations are subjected to seasonal and spatial oscillations as a result of assimilation and respiration by living organism and CO<sub>2</sub> transport through the water/atmosphere interface. Average DIC concentrations in the surface water layer range from 25–27 mg dm<sup>-3</sup> for ocean water, to 16–18 mg dm<sup>-3</sup> for some low salinity estuaries (Thomas and Schneider 1999; Key et al. 2004). The DIC forms include: dissolved CO<sub>2</sub>, present in equilibrium with unstable H<sub>2</sub>CO<sub>3</sub> that, in turn, is in equilibrium with bicarbonate and carbonate ions: HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. These components form the so-called carbonate buffer (weak acid and its salts with strong bases). Carbonate buffer balance is described with dissociation and decay constants of H<sub>2</sub>CO<sub>3</sub> (Sarmiento and Gruber 2006). Quantitative ratio of the buffer components concentrations determines pH of sea water, establishing its value at 8.2 at 35 PSU, temperature 20°C and CO<sub>2</sub> partial pressure equal to 360 ppm (Emerson and Hedges 2008).

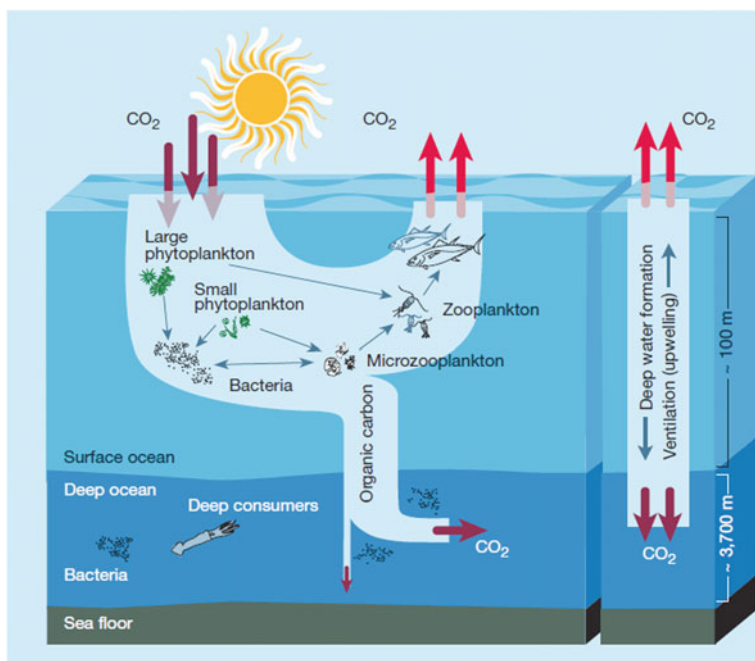
PIC consist primarily of shells and skeletons of organisms built of CaCO<sub>3</sub>. After decay of organic matter derived from the dead organisms, settling shells constitute a primary inorganic carbon carrier to the sediments (Godoi et al. 2009). However, the PIC contribution to the marine carbon pool is negligible, and its fraction is rarely distinguished for the purpose of geochemical studies (Milliman 1993; Emerson and Hedges 2008).

DOC is the measure of dissolved organic matter, and also the biggest reservoir of organic carbon on Earth (Hedges 2002). DOC consists of organic carbon in organic substances, e.g., amino acids, carbohydrates, nucleic fatty acid derivatives, humic acids, and lignin derivatives (Benner 2002). The last two groups of compounds are found particularly often in estuaries and land locked seas (Pempkowiak and Pocklington 1983; Pocklington and Pempkowiak 1984; Hedges et al. 1997). In the deep ocean, DOC concentrations remain at stable levels ranging from  $0.4 \text{ mg dm}^{-3}$  in the Pacific Ocean to about  $0.6 \text{ mg dm}^{-3}$  in the North Atlantic. The ocean surface water layer is characterized by larger variability of DOC concentrations:  $0.6\text{--}1.2 \text{ mg dm}^{-3}$  in the open ocean and  $1\text{--}6 \text{ mg dm}^{-3}$  in shelf seas (Hansell 2002; Kuliński and Pempkowiak 2008).

POC is the basic carbon carrier to the sediments (de Haas et al. 2002; Emerson and Hedges 2008). Concentrations of POC are determined mainly by the occurrence of phytoplankton and detritus, representing the largest input to the suspended organic matter. Zooplankton and bacteria contribution is much less significant (Andersson and Rudehäll 1993; Stein and Macdonald 2004). POC concentrations in sea water are some 10–20 times lower than DOC concentrations (Hansell 2002; Gardner et al. 2006), and are subject to a large spatial and seasonal variability. Concentrations, in surface waters, range from  $0.03 \text{ mg dm}^{-3}$  for oligotrophic conditions during winter season, to  $0.2\text{--}0.8 \text{ mg dm}^{-3}$  during summer season in shelf seas, characterized by high primary productivity (Gardner et al. 2006).

### 2.2.3.2 Factors Determining Carbon Cycle in the Marine Environment

The carbon cycle in the marine environment is determined by a number of physical, chemical, and biological factors that are cross-related. To a large extent, the cycle is controlled by phytoplankton activity (Dzierzbicka-Głowacka et al. 2010; Kuliński et al. 2011). Absorption and assimilation of dissolved  $\text{CO}_2$  by phytoplankton leads to disequilibria in the gas partial pressures between seawater (lower) and the atmosphere (higher), causing  $\text{CO}_2$  flux into water. On the other hand, in the course of respiration, organic substances of dead biota are oxidized to  $\text{CO}_2$ . Following the organisms death, the organic matter becomes partially mineralized in the water column and sediments, in effect balancing the loss of  $\text{CO}_2$  due to photosynthesis. The so-called biological pump refers to a series of processes including the atmospheric  $\text{CO}_2$  absorption by water,  $\text{CO}_2$  assimilation leading to organic substances that form biomass, POC mineralization in deeper water layers, and deposition of PIC and non-mineralized POC to the sediments (Fig. 2.10; Longhurst and Harrison 1989; Chisholm 2000; Honjo et al. 2008). In some regions, biological pump is strengthened by upwellings, thermohaline circulation and deep water formation. As a result of these processes, dissolved  $\text{CO}_2$  is transported to deeper layers of the water column. Because solubility of  $\text{CO}_2$  increases with decreasing temperature, while  $\text{CO}_2$  partial pressure in water decreases due to high biological productivity, the North Atlantic becomes the World Ocean region that absorbs the atmospheric  $\text{CO}_2$  most efficiently (Takahashi



**Fig. 2.10** Scheme of the biological pump processes (Chisholm 2000)

et al. 2002; Schuster et al. 2009). In a situation when  $\text{CO}_2$  partial pressure is higher in seawater than in the atmosphere, a reverse process takes place, in which the gas flows from water to the atmosphere. Such a situation is observed when respiration ( $\text{CO}_2$  production) dominate over the photosynthesis ( $\text{CO}_2$  assimilation). Upwelling zones are an example where deep water is brought up to the surface with simultaneous  $\text{CO}_2$  degassing to the atmosphere (Torres and Ampuero 2009).

An effectiveness of the biological pump depends largely on physical factors. Since solubility of the majority of gases decreases with increasing water temperature, the  $\text{CO}_2$  exchange between water and the atmosphere is determined by the water temperature (Takahashi et al. 2002). It has been demonstrated that the velocity of  $\text{CO}_2$  transport through the seawater/atmosphere interface is proportional to the cube of the wind speed (Wanninkhof and McGillis 1999).

The primary productivity—process influencing, at the same time,  $\text{CO}_2$  and DIC concentrations in a sea water—also determines organic carbon concentrations. Suspended organic matter concentrations (POC) depend directly on primary productivity (Hedges 2002). On the other hand, the intensity of primary productivity is conditioned by microelements and macronutrients dissolved in water, e.g., nutrients and iron, that are essential for organisms to function. Other factors limiting the phytoplankton growth are solar radiation and water temperature (Moore et al. 2002; Colijn and Cadée 2003; Hiscock and Millero 2002; Noiri et al. 2005). After organisms death, lyses of cells occurs and the resulting suspended organic matter

undergoes sedimentation under the influence of gravity. Its vast majority is being immediately mineralized or decomposed in the surface water layer. Hensen et al. (2006) estimated that less than 5% of the oceanic POC reaches the depth of 1,000 m. This part of POC that is actually delivered to, and deposited in the sediments participates in diagenetic processes, conditioned largely by redox potential (Frudenthal et al. 2001, Rullkötter 2006).

As a result of cells lyses, dissolved organic substances (DOC) are released to the water column. Other sources of DOC in water include its excretion by living organism, release during zooplankton sloppy feeding or during bacterial and viral infections (Carlson 2002). Most of the DOC introduced to water is biochemically unstable, and thus subjected to microbial mineralization within minutes/hours. A portion, approximately 17% of global primary productivity, is semi-stable or stable (Hansell and Carlson 1998; Lønborg et al. 2009), with residence time in the environment estimated, respectively, at weeks/years and decades/millenniums. Decomposition induced by the UV radiation, followed by the bacteria mediated mineralization and adsorption on suspended particles followed by deposition to the sediments are the primary processes that lead to DOC removal from the environment (Carlson 2002). DOC concentrations in water are also influenced by mixing processes occurring in zones where two water masses characterized by different chemical and/or biological compositions meet. The previously described upwelling and deep water formation are examples of vertical mixing as compared with horizontal mixing that includes events like wind currents, inflow of river water or water exchange between the ocean and shelf seas (Rachold et al. 2004; Thomas et al. 2005; Huertas et al. 2009).

#### ***2.2.4 Role of Shelf Seas in the Atmospheric Carbon Dioxide Absorption***

Shelf seas are coastal waters connecting the land, the atmosphere and the open ocean; their extent is usually limited to water shallower than 200 m (Thomas et al. 2009). Although the shelf seas represent about 7% of the total surface of seas and oceans, and only 0.5% of their total water volume (Chen and Borges 2009), they play an important role in the global carbon cycle. It is assumed that 20% of total organic matter originating in the marine environment is produced within shelf seas, while 80% of the total organic matter load deposited to the World Ocean sediments is deposited in the shelf seas (Borges 2005).

Significant primary production in the shelf seas is induced by high concentrations of nutrients that reach the sea with rivers draining urbanized or agricultural areas (Gattuso et al. 1998). That is why the shallower seas are believed to be regions where the biological pump processes absorbing the atmospheric CO<sub>2</sub> are more efficient than in the open ocean (Sect. 2.2.3.2; Chen and Borges 2009). Nonetheless, shelf seas are often neglected in the global biogeochemical models that estimate the role of marine environment in the anthropogenic CO<sub>2</sub> cycling



(Sabine et al. 2004). This is due to a large variability of biological, chemical and hydrological properties differentiating not only individual basins, but single shelf sea ecosystems as well. One of the examples is a difference in  $\text{CO}_2$  partial pressure of water and air. Its seasonal variation oscillates from about 40 ppm in oceanic regions to 400 ppm in shelf seas of comparable latitude (Thomas and Schneider 1999; Takahashi et al. 2002; Thomas et al. 2004). Assessment of the shelf seas role of in global  $\text{CO}_2$  cycling is a serious problem due to a limited spatial resolution of mathematical models (Bozec et al. 2006).

Tsunogai et al. (1999) presented the first available estimate for the role of shelf seas in the global cycle of anthropogenic  $\text{CO}_2$ . The authors assumed the same, as for the South China Sea, absorption capacity value for all shelf seas. Results proved that shelf seas absorb a total of  $1.0 \text{ Pg C year}^{-1}$ . Similar estimation technique was used by Thomas et al. (2004), who treated the North Sea as the global standard of  $\text{CO}_2$  transport through the seawater/atmosphere interface. The obtained net  $\text{CO}_2$  absorption was equal to  $0.4 \text{ Pg C year}^{-1}$ . The above values emphasize the importance of shelf seas, regardless of their relatively small areas, as regions absorbing carbon dioxide to the extent comparable to the ocean:  $1.6 \text{ Pg C year}^{-1}$  (Takahashi et al. 2002),  $1.7 \text{ Pg C year}^{-1}$  (Sabine et al. 2004),  $1.9 \text{ Pg C year}^{-1}$  (Sarmiento and Gruber 2006).

However, in recent years there have been expressed numerous skeptical opinions regarding the role that shelf seas actually play in the anthropogenic  $\text{CO}_2$  absorption (Andersson and Mackenzie 2004; Cai and Dai 2004; Borges 2005; Borges et al. 2005; Borges et al. 2006; Cai et al. 2006; Chen and Borges 2009). The results demonstrate that, in fact, the open water of shelf seas effectively absorbs  $\text{CO}_2$  in the amount of  $0.2\text{--}0.4 \text{ Pg C year}^{-1}$  (Borges et al. 2006; Chen and Borges 2009). However, these estimates have not included specific coastal ecosystems: estuaries, upwelling zones, mangrove forests (Chen and Borges 2009). In the meantime, scientific reports from 40 years ago demonstrated that these ecosystems emit  $\text{CO}_2$  to the atmosphere (Park et al. 1969; Kelley and Hood 1971). Chen and Borges (2009) estimated this emission at  $0.5 \text{ Pg C year}^{-1}$ . This load equalizes the  $\text{CO}_2$  absorption through the open water of shelf seas. Despite the fact that this result is charged with significant error, it gives a quite new meaning to shelf sea contribution levels in reaching the global balance of the anthropogenic  $\text{CO}_2$ . The complexity of mechanisms determining functioning of the shelf sea ecosystems results in significant errors of the estimates regarding  $\text{CO}_2$  absorption/emission. Insufficient knowledge regarding the matter cycle in shelf seas has been manifested in subsequent data reports, that significantly vary between each other, even if they concern the same areas (Chen et al. 2003; Borges et al. 2005; Chen and Borges 2009).

In the context of the examples cited above, it should be assumed that the Baltic Sea, characterized by intensive phytoplankton activity occurring from spring to fall, additionally supplied by a significant load of nutrients (HELCOM 2009), is a basin that effectively absorbs  $\text{CO}_2$ . On the other hand, extensive mineralization of organic matter generated during primary production as well as transported by river run off, will contribute significantly to  $\text{CO}_2$  production. There is a wide range of

literature data available, focusing on the CO<sub>2</sub> exchange between the Baltic and the atmosphere (Thomas and Schneider 1999; Algesten et al. 2004; Kuss et al. 2006; Omstedt et al. 2009). However, all these estimates, reporting local scale studies, still do not provide a clear answer to the question whether the Baltic Sea (as a water body) acts as a CO<sub>2</sub> emitter or absorber, and what is the magnitude of these processes?

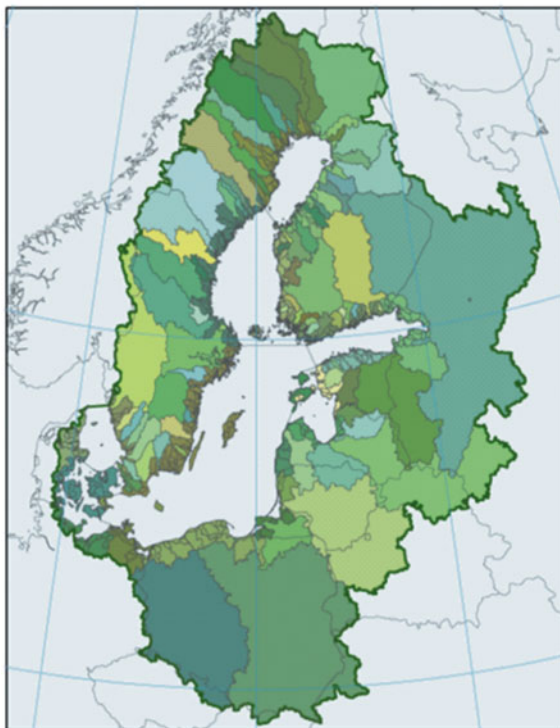
## 2.3 Carbon Cycling in the Baltic Sea

### 2.3.1 *Baltic Sea Characteristics*

The Baltic Sea is an inland shelf sea located in Northern Europe, stretching from 53 to 66°N in latitude and from 20 to 26°E in longitude. The basin occupies an area of  $3.85 \cdot 10^5$  km<sup>2</sup> (without the Kattegat) and contains a total water volume equal to  $22 \cdot 10^3$  km<sup>3</sup> (Fig. 2.11; Gudelis and Jemielianow 1982; HELCOM 2002; BACC Author Team 2008; Lass and Matthäus 2008).

Narrow and shallow Danish Straits (the Great Belt, Little Belt, Oresund—extending through the Skagerrak, and the Kattegat) are the only connection of the Baltic Sea with the North Sea. In a consequence, only infrequent incidents of horizontal water exchange of considerable volume (100–250 km<sup>3</sup>) are reported. The water inflows from the North Sea are the cause of density stratification, as well as salinity gradient occurring from the southwest to the northeast. Surface water salinity ranges from 7–8 PSU in the Arkona Deep (south-western part of the Baltic) to 2–3 PSU in the northern part of the Baltic (the Bothnian Bay). The Baltic Sea is considered to be one of the largest brackish water basins in the world. Regardless of its shallowness, inflows of saline and dense seawater from the North Sea is one of the main causes of permanent stratification in regions of the Baltic with water depth exceeding 60–80 m. The halocline, occurring at a depth of 60–80 m, separates the brackish (6–8 PSU) surface water from deeper water layers (11–15 PSU). Limited vertical mixing leads to oxygen deficits and occurrence of hydrogen sulphide. In summer this is enhanced by the thermocline present at 25–30 m and infrequent inflows of the North Sea water, rich in oxygen (Voipio 1981; HELCOM 2002; Stigebrandt 2001; Omstedt et al. 2004; Meier 2007; BACC Author Team 2008; Lass and Matthäus 2008; Matthäus et al. 2008). Significant river runoff estimated at 428 km<sup>3</sup> year<sup>-1</sup> is the largest source of fresh water in the Baltic, contributing to its brackish character. The volume of precipitation is nearly two times smaller (237 km<sup>3</sup> year<sup>-1</sup>) and compensated mainly by evaporation estimated at 184 km<sup>3</sup> year<sup>-1</sup>. The largest river runoff is delivered to the Gulf of Bothnia, the Gulf of Finland, and the Gulf of Riga. Combined the discharges are estimated at 70% of the total volume of fresh water delivered to the sea. The Baltic drainage area is over four times greater than the sea area itself, and covers the territories of fourteen countries. The catchment area is rather diverse geographically—from the mountains and forests of the Scandinavian Peninsula, characterized by a numerous small basins—to

**Fig. 2.11** The Baltic Sea drainage area with the highlighted rivers catchments (HELCOM 2007)



lowland mainland areas, transformed agriculturally. The lowland regions, covering the eastern and southern part of the Baltic drainage area, are characterized by large river basins, such as the Neva River, the Vistula River, or the Odra River (Fig. 2.11; Bergström et al. 2001; Omstedt and Axell 2003; Omstedt et al. 2004; HELCOM 2007; Meier 2007; Lass and Matthäus 2008).

The Baltic Sea is characterized by a low salinity that, coupled with the osmotic stress, leads to the ecosystem biodiversity loss expressed in decreasing number of species and the size of individual organisms. On the other hand, Baltic as a transitional area between sub-arctic conditions prevailing in the Gulf of Bothnia and boreal conditions in the southern part of the basin, is a site habitable for species characteristic for both climatic zones. Another factor that significantly shapes the Baltic Sea ecosystem is the human impact. Besides the contaminants introduced to the basin, eutrophication driven by extensive nutrient loads, originating especially from urbanized and agricultural areas, is of particular importance. It is mainly the phosphorus and nitrogen delivered with river runoff that promote the increased ecosystem productivity. In a consequence, intensive mineralization of organic matter occurs, which contributes to a spread out of anaerobic conditions, especially in the deeper water layers of the Baltic. The process of eutrophication greatly promotes the phytoplankton blooms, including toxic cyanobacteria, which additionally becomes a public health concern, especially in the

near-shore areas. A separate issue resulting from human activity is a problem of ballast water and invasive species that do influence biodiversity in various ways (Voipio 1981; Hagström et al. 2001; BACC Author Team 2008; HELCOM 2009).

### ***2.3.2 Carbon Reservoirs in the Baltic Sea***

Carbon resources estimates for the Baltic Sea are obtained by multiplying the water volume and concentration of various forms of carbon. In a situation when water volume is a relatively stable measure, carbon resources are dependent on concentrations that, in turn, are conditioned by a number of processes analogous to those observed for other basins, as described in Sect. 2.2.3.2 (e.g., Vichi et al. 2004; Omstedt et al. 2009).

Similarly to the oceans, the largest carbon resources in the Baltic are present in the form of DIC. In the northern part of the basin, DIC concentrations are subject to greater seasonal oscillations than in the open ocean or typical shelf seas (Thomas and Schneider 1999; Bozec et al. 2006; Prowe et al. 2009). DIC concentrations in the Baltic Sea surface waters range from 18–21 mg dm<sup>-3</sup> in the southwestern parts to 16–18 mg dm<sup>-3</sup> in the northern Gulf of Bothnia (Thomas and Schneider 1999).

DOC is the second largest carbon reservoir in the Baltic. Its concentrations in the surface water vary from 3.0–4.3 mg dm<sup>-3</sup> for the open waters of the Gulf of Bothnia and the southwestern parts of the Baltic to 3.5–6.5 mg dm<sup>-3</sup> for the vicinity of estuaries. The concentrations are 3–4 times higher than those reported for the open ocean water (Voipio 1981; Pempkowiak et al. 1984; Ferrari et al. 1996; Hagström et al. 2001; Algesten et al. 2006; Kuliński and Pempkowiak 2008). POC exhibits the largest relative seasonal oscillations of concentrations. This is caused primarily by intensive phytoplankton bloom events, when the POC concentration exceeds 1.0 mg dm<sup>-3</sup>. During the winter season, POC concentrations in the Baltic open water, that do not exceed 0.1 mg dm<sup>-3</sup>, are controlled mainly by the amount of slowly sinking detritus (Pempkowiak et al. 1984; Burska et al. 2005; Dzierzbicka-Glowacka et al. 2010).

### ***2.3.3 Carbon Sources and Losses in the Baltic Sea***

As a result of processes occurring in the water column (e.g., photosynthesis, respiration, sorption), carbon species transform into one another without changing the total carbon concentration. There are additional external factors that also influence carbon reservoirs in the Baltic ecosystem compartments. Depending on the resulting flux direction, the factors are classified as sources—causing the concentration increase, and losses—reducing carbon concentrations within the basin. Overview of carbon major sources and sinks in the Baltic Sea is presented in the following sections.

### 2.3.3.1 Carbon Exchange Between the Baltic and the North Sea

The Danish Straits are the only route of water exchange between the Baltic Sea and the North Sea, and further with the Atlantic Ocean. Along with the sea water masses, dissolved and suspended substances, including carbon species, are transported. The amount of carbon that is exported from, and imported to, the Baltic depends mainly on the volume of flowing water. According to various sources, as reviewed and summarized by Omstedt et al. (2004), it has been demonstrated that, on average, 1,100–2,520 km<sup>3</sup> of water is yearly discharged from the Baltic to the North Sea, while 600–1,350 km<sup>3</sup> year<sup>-1</sup> is transported in the opposite direction. These significant data differences result from a high variability of the direction and volume of flowing water masses, that are dependent on wind velocity and direction, and are often changing in a short time intervals (BACC Author Team 2008). Döös et al. (2004) estimate that only 6% of water flowing through the Great Belt resides in the Baltic for longer than a year, compared to 32% for the Oresund. Therefore, the BACC Author Team (2008) recommends the salinity to be used as an indicator allowing for water masses distinction and determination of the magnitude of flow through the Danish Straits. Despite their significant variability, the above-mentioned values indicate that the water exchange between the two basins is a decisive factor determining the Baltic Sea water balance. At the same time, the carbon exchange through the Danish Straits becomes an important aspect of the Baltic Sea carbon cycle. Based on calculations of water mass flows and their patterns (Wulff et al. 2001), coupled with an assumption of constant DIC and DOC annual concentrations in the Baltic and the North Sea water, Thomas et al. (2003) estimated that Baltic exports yearly 20 Tg C, in contrast to the yearly import amounting to just 6 Tg C. Based on these data, Thomas et al. (2005) suggested the Baltic Sea to be the largest net source of carbon for the North Sea. Moreover, both basins, combined, play the essential role in the mechanism of carbon transfer from the atmosphere and land to the deeper water of the North Atlantic.

### 2.3.3.2 Carbon Supplied With the River Runoff

Rivers are considered to be an essential element of the water balance of the Baltic Sea and important source of carbon. Pempkowiak and Kupryszewski (1980) estimated that, at least, 25% of organic matter present in the Baltic Sea has a terrestrial origin, out of which 50% is represented by humic substances, resistant to biochemical degradation (Pempkowiak and Pocklington 1983). Despite this, only few studies have focused on this group of compounds, in contrast to detailed investigations concerning nutrients (e.g., Petterson et al. 1997; Wulff et al. 2001; Granskog et al. 2005a).

River waters discharged into the Baltic are characterized by high concentrations of organic carbon (Granskog et al. 2005b). Pempkowiak (1985) has shown that DOC concentration in the lower stretch of the Vistula River ranges from 7.2 mg dm<sup>-3</sup> in winter to 9.4 mg dm<sup>-3</sup> in summer. Assuming the same DOC

concentrations for all the remaining rivers flowing into the Baltic, it was estimated that rivers bring annually a total of 3.35 Tg of organic carbon, which represents approximately 3.3% of the total DOC pool in the Baltic. Similar DOC concentrations ( $9.5 \text{ mg dm}^{-3}$ ) were observed for the Svartan River and Öre River flowing into the Gulf of Bothnia (Langenheder et al. 2003; Granskog et al. 2005b). In a contrary, Granskog et al. (2005a) recorded DOC concentrations reaching as much as  $14 \text{ mg dm}^{-3}$  for the Siikajoki River, also flowing into the Gulf of Bothnia, which situates this river among watercourses characterized by the highest DOC concentrations in the world (Cauwet 2002; Dittmar and Kattner 2003). High concentrations of organic carbon in rivers flowing into the Gulf of Bothnia make them the source of a significant carbon load for the Baltic Sea. Algesten et al. (2006) estimated that the rivers escaping into the Baltic within Finland and Sweden deliver, respectively, 0.65 and 0.85 Tg of organic carbon annually.

In contrast to numerous reports on organic carbon, the data concerning inorganic carbon in the Baltic rivers are rather limited (Pempkowiak 1985; Thomas and Schneider 1999). Alkalinity is the parameter used in river monitoring programs, that allows to estimate DIC concentration in the most accurate manner. Alkalinity is a measure of the ability of a solution to neutralize hydrogen ions, expressed in equivalent mass per unit volume. In the surface water, it is determined mainly by the presence and concentration of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ions. In the rivers escaping to the Baltic, due to pH ranging from 7.0 to 7.5, the  $\text{HCO}_3^-$  ions play the dominant role.

The Scandinavian rivers are characterized by relatively low DIC concentrations, and at the same time low alkalinity. Brink et al. (2007) determined an average alkalinity for the Kalix and Lule rivers during 1985–2003 at 0.22 and  $0.15 \text{ meq dm}^{-3}$  respectively. When assuming that alkalinity is driven by the presence of  $\text{HCO}_3^-$  the value is equal to DIC concentrations corresponding to 2.6 and  $1.8 \text{ mg dm}^{-3}$  for Kalix and Lule, respectively. The DIC present in the rivers originates mostly from the organic matter mineralization, and to a smaller extent from weathering and erosion. The authors estimate that 1.9 and  $1.2 \text{ mg DIC dm}^{-3}$ , respectively, for the Kalix and the Lule, come from mineralization of organic matter.

Thomas and Schneider (1999) obtained similar DIC concentration values (approximately  $2 \text{ mg dm}^{-3}$ ) for river discharges flowing into the Gulf of Bothnia. Relationship of DIC concentrations and salinity was determined for different parts of the open Baltic Sea water, and the correlations obtained for each zone were extrapolated to 0 PSU, giving DIC concentration in river water. For the Gulf of Finland and the Gulf of Riga, higher DIC concentrations have been estimated, amounting to 7 and  $33 \text{ mg dm}^{-3}$ , respectively. Water of the river mouth in the southern Baltic is also characterized by high DIC concentrations. Unpublished data (Beldowski, personal communication) indicate relatively constant DIC concentrations for the Świna ( $24\text{--}27 \text{ mg dm}^{-3}$ ) and well pronounced seasonal dynamics of DIC in the Vistula ( $32\text{--}45 \text{ mg dm}^{-3}$ ). Based on extrapolation method described by Thomas and Schneider (1999), and DOC average concentration of  $4.3 \text{ mg dm}^{-3}$ , it has been estimated (Thomas et al. 2003) that continental rivers supply the Baltic

Sea with 4.9 Tg C per annum. This value represents approximately 35-fold higher carbon load than that estimated for the Scandinavian rivers (0.12 Tg C year<sup>-1</sup>; Thomas et al. 2003).

### 2.3.3.3 Carbon Deposition to the Sediments

POC plays a dominant role in carbon transport to the sea floor, while it is assumed that the role of PIC is minimal and falls within the error limits (Zsolnay 1973; Schneider et al. 2000; Struck et al. 2004). Carbon deposition depends on a number of processes taking place in a water column and sediments. The amount and quality of the material that can, potentially, sink to the bottom is the most significant factor. The main sources of organic matter containing particles suspended in the water column are the primary productivity and fluvial processes. As a result of mineralization and decomposition, only a small fraction of the suspended matter reaches the sediments, and the actual deposition location is determined by hydrological factors (Voipio 1981; Blomqvist and Heiskanen 2001).

The primary productivity magnitude in the Baltic changes spatially and temporarily. Nutrients are the driving force for primary productivity: the Gulf of Bothnia is the least active basin in this respect, while the greatest primary productivity is observed for the Gulf of Riga and the south-western part of the Baltic (Table 2.1; Voipio 1981; Wasmund et al. 2001; HELCOM 2009).

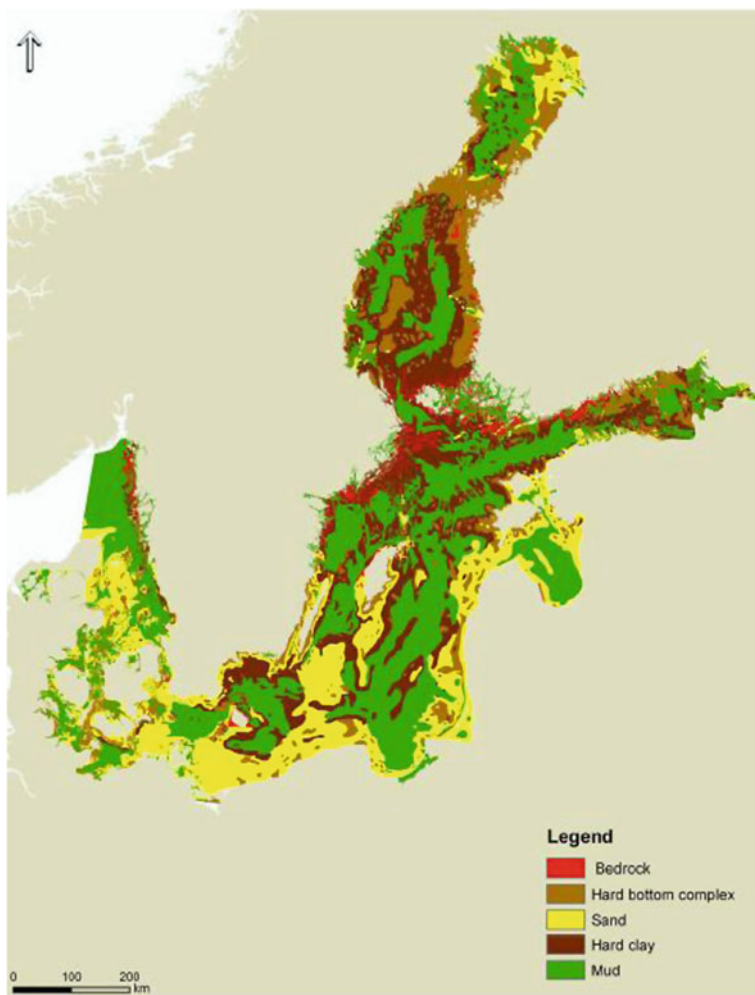
The comparison of data on the primary productivity, as summarized by Wasmund and Siegel (2008), revealed the significant increase in the last decades in the southern parts of the Baltic and in the Gulf of Riga, while no significant changes have been reported for the Gulf of Bothnia (Table 2.1). The largest increase (nearly threefold) was observed in the Gulf of Riga, somewhat smaller (approximately twofold) in the Danish Straits and the so-called Baltic Proper. Changes in the magnitude of primary productivity for the entire basin lead to its overall increase from 84 g m<sup>-2</sup> year<sup>-1</sup> in the late 1970s and 1980s to 150 g m<sup>-2</sup> year<sup>-1</sup> presently.

**Table 2.1** Primary productivity in the Baltic Sea (Wasmund and Siegel 2008 based on Kaiser et al. 1981 and Wasmund et al. 2001)

Region	Primary productivity (g C m <sup>-2</sup> year <sup>-1</sup> )	
	Kaiser et al. (1981)	Wasmund et al. (2001)
Kattegat/Danish straits	90–120	190
Proper Baltic	90–125	200
Gulf of Riga	80–100	261
Gulf of Finland	70	82
Bothnian Sea	70	52
Gulf of Bothnia	18	17
Baltic Sea—average	84	150



Organic carbon is deposited mainly in areas of fine-grained sediments (mud-clay) covering 32% of the Baltic Sea bottom (Fig. 2.12; Emeis et al. 2000; Al-Hamdani and Reker 2007). This type of sediments is characterized by high organic carbon concentrations, reaching 10–11% in the uppermost sediment layers. Such high concentrations result from sedimentation of material that is rich in organic matter, and the permanent oxygen deficit in the sediments. The absence of oxygen slows down the mineralization rate of organic matter. The regions characterized by oxygen deficit and substantial sedimentation include: the Gotland Deep, the Gdansk Deep and the Bornholm Deep, where more than 50% of the Baltic total organic matter is deposited (Emeis et al. 2000). Areas of sea bottom



**Fig. 2.12** The Baltic Sea sediment types (Al-Hamdani and Reker 2007)

covered by other sediment types play a minor role as accumulation areas of sedimentary material in the Baltic, and the majority of organic matter reaching their surface is subjected to rapid mineralization or resuspension and relocation to the depositional areas. This is best indicated by low concentrations of organic carbon within the uppermost sediment layers: 0.05–0.5% of dry weight (d.w.; Maksymowska 1998).

Studies involving sediment traps conducted in the Gotland Deep (Struck et al. 2004) revealed that POC transport to the sediments at a depth of 140 m amounts to  $6.0 \text{ g m}^{-2} \text{ year}^{-1}$ . Summer and autumn carbon fluxes contribute most significantly to the annual POC flux: 31.9% and 34.6%, respectively. Slightly higher levels of POC transport to the sediments (also assessed using sediment traps) obtained by Schneider et al. (2000) were calculated to be  $7.9 \text{ g m}^{-2} \text{ year}^{-1}$ . Based on this value, assumed to be the same for the Baltic Proper, the Gulf of Finland and the Gulf of Riga, Schneider et al. (2000) estimated that 1.7 Tg C is deposited in these regions every year.

The total organic carbon (TOC) accumulation rate in the bottom sediments is calculated based on the designated sedimentation rate, usually assessed using a method based on  $^{210}\text{Pb}$  activity, as well as organic carbon concentration levels in the sediments. Algesten et al. (2006) estimated, based on the accumulation rate of TOC for the uppermost sediment layers, that 1.1 Tg C is deposited in the Gulf of Bothnia annually. On the other hand, Emeis et al. (2000) indicate that TOC accumulation rates in the Bornholm Deep, Gdansk Deep, and Gotland Deep increased two- to three-fold during the several last decades, while current values amount to  $60 \text{ g C m}^{-2} \text{ year}^{-1}$ ,  $60\text{--}65 \text{ g C m}^{-2} \text{ year}^{-1}$  and  $40 \text{ g C m}^{-2} \text{ year}^{-1}$ , respectively. Only in the vicinity of Arkona Deep, organic carbon accumulation rates remain at a constant level ranging from 20 to  $25 \text{ g C m}^{-2} \text{ year}^{-1}$ . The suggested increase of TOC accumulation rates is attributed to a greater organic matter influx to the sediments and transformations of environmental conditions determining organic matter degradation processes (Emeis et al. 2000; Struck et al. 2000; Szczepanska et al. 2011). This opinion is also confirmed by Jonsson and Carman's (1994) studies that estimated close to twofold increase of TOC accumulation rates in the Gulf of Bothnia in the 1980s, compared to the 1920s. For the Baltic Proper, this increase has been estimated to be five to ten times higher than the historical one.

#### 2.3.3.4 Carbon Dioxide Exchange at the Water/Atmosphere Interface

The Baltic Sea is a diverse ecosystem. The basin consists of regions characterized by a low primary productivity and large terrestrial organic matter inflow (the Gulf of Bothnia), through highly productive areas, located in the central and southern part of the basin, to highly eutrophic regions specific for the main rivers mouths (Voipio 1981; Hagström et al. 2001; Nausch et al. 2008; Wasmund and Siegel 2008). This situation is reflected in the direction and rate of  $\text{CO}_2$  exchange through the water/atmosphere interface.

The Gulf of Bothnia is considered to be a source of CO<sub>2</sub> to the atmosphere, which is attributed to intensive mineralization of organic matter supplied to the Gulf with the river runoff and limited, especially when compared with the southern Baltic, phytoplankton activity (Algesten et al. 2004 and Algesten et al. 2006). It has been estimated (Algesten et al. 2004) that the Gulf of Bothnia annually releases 3.79 Tg C in the form of CO<sub>2</sub>, which corresponds to 37.2 g C m<sup>-2</sup>. Subsequent estimates concerning CO<sub>2</sub> cycling in the Gulf of Bothnia were similar. Algesten et al. (2006) calculated carbon emission for the entire Gulf at the level of 3.61 Tg C year<sup>-1</sup>, which corresponds to specific emissions of 35.4 g C m<sup>-2</sup> year<sup>-1</sup>.

In contrast to the Gulf of Bothnia, the remaining portion of the Baltic Sea is considered to absorb atmospheric CO<sub>2</sub> (Ohlson 1990; Thomas and Schneider 1999; Kuss et al. 2006). Ohlson (1990) estimated the average atmospheric CO<sub>2</sub> uptake at 13.2 g C m<sup>-2</sup> year<sup>-1</sup>. Thomas and Schneider (1999) obtained comparable results, and based on biogeochemical model the authors calculated that the so-called Baltic Proper (Baltic without the major gulfs: Bothnia, Finland, Riga and Danish Straits) absorbs  $10.8 \pm 1.1$  g C m<sup>-2</sup> year<sup>-1</sup>. In the southern Baltic, the Arkona Deep is of special interest; buoy-based measurements of partial pressure of dissolved CO<sub>2</sub> in water are available for this location (Kuss et al. 2006). The results indicate that this region is characterized by carbon dioxide absorption amounting to 36.0 g C m<sup>-2</sup> year<sup>-1</sup>.

### 2.3.3.5 Other Sources and Losses of Carbon in the Baltic Sea

Additional sources of carbon in the Baltic Sea include precipitation and the so-called point sources (HELCOM 2004; Algesten et al. 2006). These consist of all terrestrial carbon inflows, other than river runoff. Wastewater treatment plants located along the shoreline are the main source (70%) here (HELCOM 2004). The data indicate that annually 3.6 km<sup>3</sup> of treated sewage is discharged to the Baltic. Organic carbon load delivered from the point sources is frequently expressed as the seven-day biochemical oxygen demand (BOD<sub>7</sub>). This, for the entire Baltic Sea, is calculated to be 88.7 Gg O<sub>2</sub>. Converted to the carbon load, using a BOD<sub>7</sub>/C<sub>org</sub> ratio of 2.28 (HELCOM 1983), this corresponds to 39 Gg C, half of which is delivered to the Gulf of Bothnia. Industrial plants, associated mainly with paper and timber industry, contribute 65% of the total organic carbon inflow from the point sources. To a smaller extent, supply from point sources includes municipal wastewater (33%) and fish farms (2%).

Precipitation constitutes an important freshwater source for the Baltic Sea. However, the literature data lack concentrations of organic and inorganic carbon in the rainwater within the Baltic. Based on the data presented by Anttila et al. (1995) and Algesten et al. (2006) the estimated amount of organic carbon reaching the Gulf of Bothnia with rainwater at 0.11 Tg year<sup>-1</sup>.

On the other hand, fisheries cause carbon depletion in the Baltic. Since fish tissue comprise significant amounts of organic carbon, it can be regarded as a reservoir of carbon. Herring (*Clupea harengus membras*) and sprat (*Sprattus sprattus*) are the

most commonly harvested species—presently contributing over 80% of the total catch. Fish harvested to a smaller extent include cod, flounder, salmon and freshwater species (Hammer et al. 2008; ICES 2008). According to the ICES report (ICES 2008), the catch magnitude in the period 1974–1984 oscillated at a level of  $850\text{--}990\ 10^3\ \text{ton year}^{-1}$ , increasing during 1996–1998, primarily due to cod catch, to  $1,100\ 10^3\ \text{tons year}^{-1}$ . ICES (2008) estimates the current Baltic Sea annual catch to be  $700\ 10^3\ \text{ton fish year}^{-1}$ . Assuming 8.2% as an average carbon concentration in a wet fish tissue (Crabtree 1995), this corresponds to carbon extraction from the Baltic equal to  $57\ \text{Gg C year}^{-1}$ .

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