Impacts of Global Warming on Biogeochemical Cycles in Natural Waters

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1 Introduction

The main source of energy that drives the dynamics of Earth's outer spheres, including its climate, is unquestionably the Sun (Kandel and Viollier 2005). Therefore, electromagnetic radiation enormously dominates the energy exchange between the Earth and its cosmic environment (Kandel and Viollier 2005). At a radiative balance of 235 W m^{-2}, the Earth would have an average surface temperature of only −19 °C, resulting in a perpetually frozen planet (Ruddiman 2001). Fortunately, the planetary atmosphere traps sufficient long-wave energy that is reradiated by the warm Earth's surface (greenhouse effect) to raise the surface temperature by approximately 33 °C to a more hospitable average of 14 °C (Ferguson and Veizer 2007). The greenhouse effect is efficiently caused by the

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K. M. G. Mostofa et al. (eds.), *Photobiogeochemistry of Organic Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-32223-5_10,

occurrence of the atmospheric greenhouse gases (GHGs), the main one being water vapor (H_2O) followed to a lesser extent by CO_2, CH_4, N_2O, CFCs and so on (Wigley 1988, 1989; Charlson et al. 1989; Fisher et al. 1990; den Elzen et al. 1992; Kroeze and Reijnders 1992; Solomon and Daniel 1996; Kiehl and Trenberth 1997; Quaas et al. 2004; IPCC 2007a; Velders et al. 2007; May 2008; Schmidt et al. 2010; Zhang et al. 2011). A typical definition of global warming is an increase of the global average temperatures at the interface between Earth's near surface air and water. It is generally caused either by the absorption of long-wave (or thermal) infrared radiation by the GHGs and other atmospheric constituents or by high penetration of short-wave, e.g. ultraviolet (UV) radiation due to the depletion of the stratospheric ozone layer caused by ozone depleting substances.

GHGs and other atmospheric constituents are substantially released by increased soil respiration processes (Bradford et al. 2008; Bahn et al. 2010; Feng et al. 2010), high agricultural activities in soils (Mosier et al. 2004; Robertson and Grace 2004; Ambus and Robertson 2006; Smith et al. 2008), anthropogenic processes (IPCC 2007a; Sabine et al. 2004; Smith 2004; Archer 2005; Canadell et al. 2007; Hofmann et al. 2009), deforestation (IPCC 2001, 2007a; Kreileman and Bouwman 1994; van der Werf et al. 2009), photoinduced and microbial degradation of aquatic organic matter (OM) including dissolved organic matter (DOM) and particulate organic matter (POM) (Bozec et al. 2005, 2006; Schiettecatte et al. 2006, 2007; Borges et al. 2008; Omar et al. 2010; Ballaré et al. 2011; Zepp et al. 2011), and photoinduced and microbial degradation of OM in plants and soil environments (Brandt et al. 2009; Rutledge et al. 2010).

On the other hand, global warming significantly affects various biogeochemical processes of natural waters, including changes in light cycle, increase of water temperature (O'Reilly et al. 2003; Letelier et al. 2004; Huisman et al. 2006; Porcal et al. 2009), enhancement of the photoinduced activity of aquatic DOM and OM (Hiriart-Baer and Smith 2005; Molot et al. 2005; Johannessen et al. 2007; Mostofa and Sakugawa 2009; Mostofa et al. 2009a, b, 2011), changes in the microbial processing of aquatic DOM and OM (Norf et al. 2007; Vázquez-Domínguez et al. 2007; Falkowski and Oliver 2008; Peters 2008; Norf and Weitere 2010; Sarmento et al. 2010; Sawicka et al. 2010), enhancement of photosynthesis(Mostofa et al. 2009b; Marcoval et al. 2008; Zubkov and Tarran 2008; Beardall et al. 2009a, b), changes in the primary productivity (Huisman et al. 2006; Mostofa et al. 2009b; Baulch et al. 2005; Castle and Rodgers 2009; Davis et al. 2009), changes in the aquatic DOM dynamics and global carbon cycles (Zepp et al. 2011; Porcal et al. 2009; Burns et al. 2006; Vuorenmaa et al. 2006; Sobek et al. 2007; Zhang et al. 2010), and changes in the nutrients cycle (Mostofa et al. 2009b; Fu et al. 2005; Minero et al. 2007; Stedmon et al. 2007a, b; Sterner et al. 2008).

The effects of ambient levels of UV radiation (UV-B: 280–315 nm and UV-A: 315–400 nm) can alter both planktonic and benthic communities within the biota of alpine lakes (Cabrera et al. 1997; Halac et al. 1997; Sommaruga et al. 1997, 1999a; Vinebrooke and Leavitt 1998; Sommaruga and Garcia-Pichel 1999). The impact of UV radiation may interact with other important environmental changes affecting high-latitude and high-altitude lakes, such as acidification and climate warming (Vinebrooke and Leavitt 1998; Schindler et al. 1996; Yan et al. 1996; Sommaruga et al. 1999b). UV-B radiation strongly influences aquatic carbon, nitrogen, sulfur and metals cycles and affects a wide range of life processes (Epp et al. 2007). UV-B radiation changes the biological availability of dissolved organic matter (DOM) to microorganisms and accelerates DOM transformation into dissolved inorganic carbon and nitrogen, including carbon dioxide and ammonium (Epp et al. 2007). It is reported that large shifts in underwater UV-B, UV-A and photosynthetically available radiation (PAR) associated with changes in the input of colored DOM occurred into subarctic lakes during the Holocene (Pienitz and Vincent 2000). A moderate increase in UV-B also occurred in the northern hemisphere such as in the Arctic (von Der Gathen et al. 1995) and in the Swiss Alps (Blumthaler and Ambach 1990).

Global warming induces changes of climate, soil and water ecosystems (IPCC 2007a). Some 70 % of the Earth surface is covered by water containing an extremely complicated milieu of organic and inorganic chemical species (Erickson Iii et al. 2000). The photoinduced production and transformation of various greenhouse and chemically reactive gases in the ocean has been a focus of many studies over the last century (Erickson Iii et al. 2000). Increased UV radiation has implications on the biogeochemistry of the aquatic and marine boundary layer, with a focus on trace gases such as CO_2, DMS, CO, OCS, CH_4, N_2O, non-methane hydrocarbons (NMHCs) and organohalogens, which can be exchanged between the ocean and the atmosphere (Erickson Iii et al. 2000).

This chapter describes a general overview on the contributions to global warming of atmospheric constituents including GHGs, as well as their key emission processes. The aim of this review is to explain the impacts of global warming on the aquatic biogeochemical processes, including changes in light cycle and water temperature, photoinduced processes, microbial processes, photosynthesis, primary production, dissolved organic matter (DOM) dynamics and global carbon cycle, and finally the nutrients cycle in natural waters. This chapter also discusses a conceptual model for the effect of global warming on key biogeochemical processes and remedial measures for controlling algal blooms caused by global warming.

2 Global Warming

The atmospheric constituents accountable for global warming are: water vapor; clouds (condensed water in ice and liquid form); greenhouse gases (GHGs) such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and halocarbons including chloroflurocarbons (CFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), ozone, sulphur hexafluoride (SF_6), methyl chloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4) (Wigley 1988, 1989; Charlson et al. 1989; Fisher et al. 1990; den Elzen et al. 1992; Kroeze and Reijnders 1992; Solomon and Daniel 1996; Kiehl and Trenberth 1997; Quaas et al. 2004; IPCC 2007a; Velders et al. 2007; May 2008; Schmidt et al. 2010; Zhang et al. 2011; Robertson and Grace 2004; Friedlingstein et al. 2003; Jones et al. 2003a, b, c; Le Quéré et al. 2003; Archer et al. 2004; Buffett and Archer 2004; Forster and Joshi 2005; Hansen and Sato 2004; Eliseev et al. 2007). Atmospheric constituents are responsible for increasing the atmospheric temperature via two main processes. First, long-wave (or thermal) radiation emitted from the terrestrial surface is absorbed at a particular frequency and reemitted at lower frequency by greenhouse gases and clouds throughout the earth's atmosphere. The earth's surface can emit long-wave (or thermal) radiation because it is heated by sunlight. Second, gases, clouds and aerosols can absorb and scattered short-wave radiation (UV and visible) significantly. The cooling effect via short-wave reflection is dominant for clouds and aerosols. The transfer of long-wave radiation depends on both the local temperature of the gaseous absorber and the efficiency of the gases to absorb radiation at a given wavelength (Kiehl and Trenberth 1997). The absorption efficiency varies with wavelength. Note that many greenhouse gases can absorb radiation at the same wavelengths, which is called the overlap effect. In the presence of clouds, the transfer of radiation depends on the cloud amount, on the efficiency of clouds to absorb and reemit the long-wave radiation (cloud emissivity) and on the cloud top and base temperatures (Kiehl and Trenberth 1997).

It has been shown that the sulfate aerosols have a negative forcing effect that partially counterbalances the warming effect of greenhouse gases (Charlson et al. 1989; Wigley 1989; Quaas et al. 2004; IPCC 2007a; Schmidt et al. 2010; Joshi et al. 2003; Eliseev et al. 2007; Rosenfeld 2000). It is suggested that aerosols scatter sunlight and enhance the planetary short-wave albedo, an effect known as the 'aerosol direct effect' (ADE). In addition, by their ability to act as cloud condensation nuclei, (hygroscopic) aerosols change cloud properties and produce essentially an increase in cloud albedo. These processes are called 'aerosol indirect effect' (AIE).

The increase in greenhouse gas concentration could lead to a reduction of clouds at all atmospheric levels, thus decreasing the total greenhouse effect in the long-wave spectrum but increasing absorption of solar radiation upon reduction of cloud albedo (Quaas et al. 2004). Increasing anthropogenic aerosols result in a decrease of high-level cloud cover by cooling of the atmosphere, and an increase in the low-level cloud cover through the second aerosol indirect effect (Quaas et al. 2004). The decrease of the high-level cloudiness and the increase of the low-level one due to the response of cloud processes to aerosols have a contrasting impact on the short-wave radiation, and the net effect is slightly positive (Quaas et al. 2004). The total aerosol effect, including the aerosol direct and first indirect effects, remains strongly negative (Quaas et al. 2004; IPCC 2007a).

In addition, the depletion of stratospheric ozone caused by atmospheric anthropogenic GHGs can enhance penetration of harmful UV-B radiation (280–315 nm), which can have a direct influence on living organisms and also affect the global warming (IPCC 2001; Huisman et al. 2006; Kerr and McElroy 1993; Varotsos and Kondratiev 1995; Hartmann et al. 2000; Qian et al. 2001; Sarmiento et al. 2004; Schmittner 2005). The impact of UV-B radiation on global warming is of two kinds. The first is a direct heating effect of UV-B radiation penetrating in the troposphere. The second effect is the release of CO_2 to the atmosphere upon photoinduced degradation of DOM induced by UV-B radiation in natural waters (Qian et al. 2001; Sarmiento et al. 2004; Schmittner 2005). However, the observed losses in the stratospheric ozone layer over the past two decades have caused a negative climate forcing (0.15 ± 0.1 Wm^{-2}), i.e. a tendency toward cooling of the surface troposphere system (IPCC 2001). Model calculations indicate that increased penetration of ultraviolet radiation to the troposphere, as a result of stratospheric ozone depletion, leads to enhanced removal rates of gases like CH_4, with a resulting cooling effect (IPCC 2001).

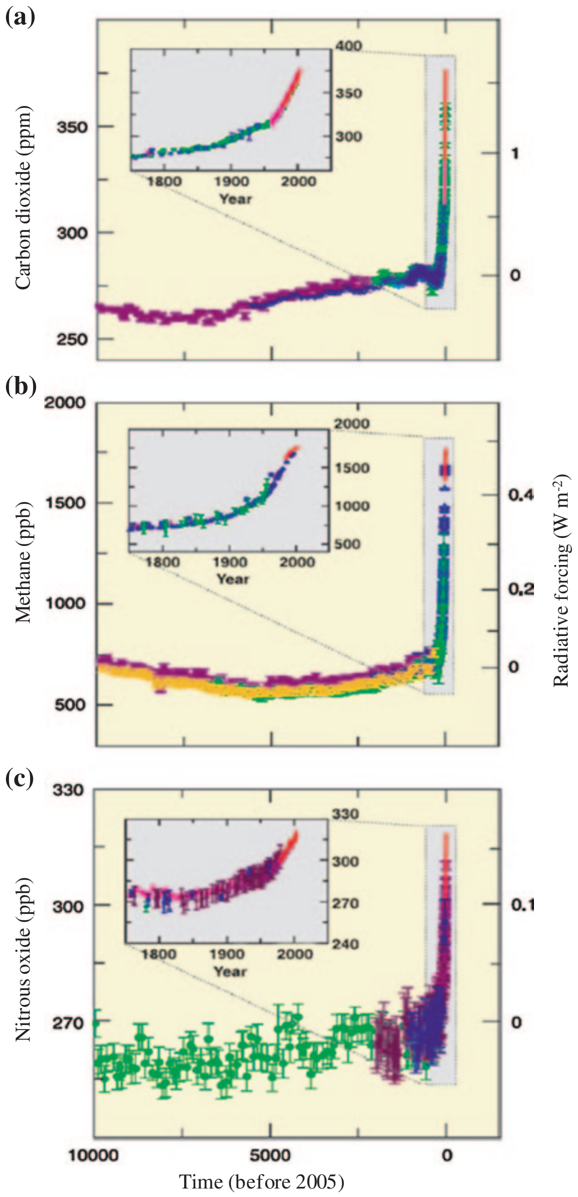
In contrast, other studies suggest that stratospheric ozone depletion and GHG warming may both be producing increased meridional temperature gradients in the extratropical lower stratosphere and upper troposphere, thereby acting synergistically to produce surprisingly large trends in both surface and stratospheric climate (Hartmann et al. 2000).

2.1 Occurrence and Contribution of Atmospheric Constituents to Global Warming

The global atmospheric concentration of CO_2 has increased from a pre-industrial value of about 280–379 ppm in 2005 (IPCC 2007a). The CO_2 concentrations in 2005 exceeded by far the natural range over the last 650,000 years (Fig. 1a) (IPCC 2007a). Despite the year-to-year variation of CO_2 concentration growth rate, it is estimated that the annual rate of CO_2 concentration growth has been larger over the past 10 years (1995–2005; average: 1.9 ppm per year) than in the whole record of continuous direct atmospheric measurements (1960-2005; average: 1.4 ppm per year). The atmospheric concentrations of CH_4 in 2005 exceeded by far the natural range over the last 650,000 years (Fig. 1b) (IPCC 2007a). The global atmospheric concentration of CH_4 increased from a pre-industrial value of about 715–1732 ppb in the early 1990s, then to 1774 ppb in 2005 (IPCC 2007a). The data also suggest that the growth rates have declined since the 1990s, coherently with total emissions (sum of anthropogenic and natural sources) being nearly constant during this period. The global atmospheric N_2O concentration increased from a pre-industrial value of about 270 ppb to 319 ppb in 2005 (Fig. 1c) (IPCC 2007a).

An important greenhouse gas in both the stratosphere and the troposphere is ozone (O_3), which is formed in the atmosphere from photoinduced processes that involve both natural and human-influenced precursor species (IPCC 2001). The residence time of ozone in the atmosphere is relatively short, varying from weeks to months (IPCC 2001). The total amount of O_3 in the troposphere is estimated to have increased by 36 % since 1750, due primarily to anthropogenic emissions of several O_3-forming gases (IPCC 2001). It is also suggested that O_3 climate forcing varies considerably depending on the region and that it responds more quickly to changes in emissions than the long-lived greenhouse gases, such as CO_2.

Fig. 1 Atmospheric concentrations of CO_2 (**a**), CH_4 (**b**) and N_2O (**c**) over the last 10,000 years (large panels) and since 1750 (inset panels). Measurements are shown from ice cores (symbols with different colours for different studies) and atmospheric samples (*red lines*). The corresponding radiative forcings relative to 1750 are shown on the right hand axes of the large panels. *Data source* IPCC (2007a)



Halocarbons have increased from a near-zero pre-industrial background concentration, and the increase is primarily due to human activities. The atmospheric concentrations of many halocarbon gases with ozone depleting and global warming potential (e.g. $CFCl_3$ and CF_2Cl_2) have been either increasing more slowly or even decreasing since 1995. This happened in response to reduced emissions

Table 1 Atmospheric lifetime and GWPs relative to CO_2 at different time horizon for various green house gases

Atmospheric gases	Global warming potentials (GWPs) (Time horizon in years)			Lifetime (yrs)
	20 yrs	100 yrs	500 yrs	
Carbon dioxide (CO_2)	1	1	1	~5–200[b]
Methane[a] (CH_4)	62	23	7	12[c]
Nitrous oxide (N_2O)	275	296	156	114[c]
Hydrofluorocarbons				
HFC-23 (CHF_3)	9400	12000	10000	260
HFC-32 (CH_2F_2)	1800	550	170	5.0
HFC-41 (CH_3F)	330	97	30	2.6
HFC-125 (CHF_2CF_3)	5900	3400	1100	29
HFC-134 (CHF_2CHF_2)	3200	1100	330	9.6
HFC-134a (CH_2FCF_3)	3300	1300	400	13.8
HFC-143 (CHF_2CH_2F)	1100	330	100	3.4
HFC-143a (CF_3CH_3)	5500	4300	1600	52
HFC-152 (CH_3CHF_2)	140	43	13	0.5
HFC-152a (CH_3CHF_2)	410	120	37	1.4
HFC-161 (CH_3CH_2F)	40	12	4	0.3
Fully fluorinated gases				
SF_6	15100	22200	32400	3200
CF_4	3900	5700	8900	50000
C_2F_6	8000	11900	18000	10000

GWPs are an index for estimating relative global warming contribution due to atmospheric emission of a kg of a particular greenhouse gas compared to emission of a kg of carbon dioxide. *Data source* IPCC (2001)

[a] The methane GWPs include an indirect contribution from stratospheric H_2O and O_3 production

[b] No single lifetime can be defined for CO_2 because of the different rates of uptake by different removal processes

[c] The values for methane and nitrous oxide are adjustment times, which incorporate the indirect effects of emission of each gas on its own lifetime

under the regulations of the Montreal Protocol and its Amendments (IPCC 2001). The halocarbon substitute compounds (e.g. CHF_2Cl and CF_3CH_2F) and some other synthetic compounds such as perfluorocarbons and sulphur hexafluoride, SF_6, are also greenhouse gases. Their concentrations are currently increasing (Table 1) (IPCC 2001).

Atmospheric sulfate aerosols have increased sharply during the past one-and-a-half centuries or so, with an overall increase in sulfate emissions from 1 Mt S in 1850 to 70 Mt S in the 1990s. Sulfate aerosols are mostly concentrated in the Northern Hemisphere, with distinct concentration maxima near major polluted regions (Lefohn et al. 1999; Smith et al. 2001). Carbon monoxide (CO) is identified as an important indirect greenhouse gas, which acts as a $HO^{\bullet}$ sink (thereby enhancing the lifetime of many direct greenhouse gases) and is involved in the formation of tropospheric O_3. A model study indicates that the emission of 100 Mt

CO is equivalent in terms of greenhouse gas perturbations to the emission of about 5 Mt CH_4 (IPCC 2001). The abundance of CO in the Northern Hemisphere is about twice that in the Southern Hemisphere and has increased in the second half of the twentieth century along with industrialisation and population growth (IPCC 2001). The reactive nitrogen species (NO and NO_2) and the volatile organic compounds, because of their impact over the oxidising capacity of the troposphere, may act as indirect greenhouse gases both through their influence on ozone and by impacting the lifetimes of CH_4 and other greenhouse gases via $HO^\bullet$ scavenging, although this latter effect is compensated for to a variable extent by the $HO^\bullet$ generation upon O_3 photolysis (IPCC 2001).

The contributions of different anthropogenic greenhouse gases to the 2004 total emissions in terms of CO_2 equivalents have been 56.6 % from fossil fuel use, 17.3 % from deforestation and decay of biomass, 2.8 % from other sources, 14.3 % from CH_4, 7.9 % from N_2O, and 1.1 % from fluorine gases (IPCC 2007a). The contributions of the different activity sectors to the total emissions of anthropogenic greenhouse gases in 2004, in terms of CO_2 equivalents are 25.9 % for energy supply, 19.4 % for industry, 17.4 % for forestry, 13.5 % for agriculture, 13.1 % for transport, 7.9 % for residential and commercial building purposes, and finally 2.8 % for waste and wastewater treatment (IPCC 2007a). In addition, recent studies shows that CO_2 can be significantly released to the atmosphere from other sources such as the photoinduced and microbial degradation of DOM and POM (e.g. algae or phytoplankton) in natural waters (Bozec et al. 2005, 2006; Schiettecatte et al. 2006, 2007; Borges et al. 2008; Omar et al. 2010; Kelley 1970; Kempe and Pegler 1991; Hoppema 1990, 1991; Borges and Frankignoulle 1999, 2002a, b). Also the photoinduced and microbial degradation of OM in terrestrial plant masses can release CO_2 to the atmosphere (Rutledge et al. 2010; Johannessen et al. 2007).

Among the atmospheric absorbers of long-wave radiation, H_2O vapor, clouds, CO_2, CH_4 and O_3 dominate while the aerosols and other species make small contributions to the overall effect (Schmidt et al. 2010). It has been shown that the contributions of atmospheric greenhouse gases (GHGs) to global warming are significantly variable depending on the occurrence of the atmospheric constituents and on the long-wave and short-wave fluxes under clear, cloudy or all-sky conditions (Kiehl and Trenberth 1997; IPCC 2007a; Schmidt et al. 2010).

The contributions of atmospheric GHGs to global warming are 39–70 % for H_2O vapor, 15–36 % for clouds, 14–31 % for CO_2, 8–18 % for O_3, and 6–9 % for other constituents including CH_4 and N_2O (Kiehl and Trenberth 1997; Schmidt et al. 2010; Harrison et al. 1990; IPCC 1990; Clough and Iacono 1995). In addition, the atmospheric short-wave (UV–Vis) absorbers are mostly H_2O vapor (38–43 W m^{-2}), O_3 (14–15 W m^{-2}), and O_2 (2 W m^{-2}) under both clear and cloudy conditions. In contrast, CO_2 (1 W m^{-2}) only gives a small contribution under clear-sky conditions (Kiehl and Trenberth 1997). It has also been shown that the all-sky contribution of water vapor and clouds together is approximately 72–80 % after removing all the other absorbers (Schmidt et al. 2010).

The direct emission of water vapor (a greenhouse gas) by human activities makes a negligible contribution to the radiative forcing, but an increase in global average temperature can enhance the tropospheric water vapor concentration and produce a key positive feedback for radiative forcing, thereby leading to further warming (IPCC 2007a). Interestingly, the so-called Humic-like Substances (HULIS) occurring on atmospheric aerosols can enhance water uptake and increase the role of particles as Cloud Condensation Nuclei (CCN), thereby contributing to direct and indirect climate forcing (Hatch et al. 2009). Warming also reduces terrestrial and ocean uptake of atmospheric CO_2, increasing the fraction of anthropogenic emissions that remain in the atmosphere. Such an effect is expected to lead to higher atmospheric CO_2 levels that are further involved into the global climate change (IPCC 2007a). The uptake by the oceans is approximately 25 % of the annual carbon emissions that result from fossil fuel burning and cement manufacturing (Canadell et al. 2007).

The infrared absorption cross-sections for eight commonly used CFCs (halogenated methanes and ethanes), as a function of temperature from 203 to 293 K, suggest that the combined effects of absorption by CFCs of the Earth's radiative energy in the 'window' region (700–1300 cm^{-1}) and of their O_3 depletion potential makes these compounds significant contributors to global warming (McDaniel et al. 1991). On the other hand, the sulfate aerosols can reduce global warming by about 0.1–0.4 K, depending on the scenario and on the time period. The maximum slowdown in warming (>1.5 K) is expected to occur in the Northern Hemisphere middle- and high-latitude land areas in the mid-twenty-first century (Eliseev et al. 2007). A recent study has shown that the indirect effect of stratospheric ozone depletion could have offset up to half of the predicted past increase in surface temperature that would otherwise have occurred as a result of the direct halocarbon effects (Forster and Joshi 2005). In both the troposphere and stratosphere, CFC-12 contributed most to the CFCs-related past temperature changes, and the emission projections suggest that HFC-134a could contribute most to the warming by halocarbons over the coming century (Forster and Joshi 2005).

2.2 Global Warming Determination

The radiative forcing (expressed in Watts per square metre, W m^{-2}) is one of the primary issues associated with potential global warming constituents (IPCC 1990, 1994, 2001). Radiative forcing is a change of the net irradiance at the top of the troposphere because of modifications in either solar or infrared radiation. Such forcing perturbs the balance between incoming and outgoing radiation (IPCC 1990, 1994). Radiative forcing is a measure of the influence of a particular factor on the balance of incoming and outgoing energy in the Earth-atmosphere system, and it is also an index for a potential climate change mechanism (IPCC 2007a). A positive radiative forcing tends to warm the climatic system while the negative forcing has a cooling effect.

The global-mean radiative forcing (ΔF) is approximately related to the equilibrium global-mean surface temperature change (ΔT) by (IPCC 1994) (Eq. 2.1):

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

where λ is the climate sensitivity parameter. Although there is a large discrepancy in the actual value of λ in different models, its values are assumed to be approximately independent of the agent causing the forcing. The spread in the model estimates of λ varies from about 0.4–1.2 K (W m^{-2})$^{-1}$, that is, approximately by a factor of 3 (IPCC 1990, 2001). The models also indicate generic deviations of λ from the case of global CO_2 perturbations: increases of O_3 in the upper troposphere generally produce lower values of λ, while O_3 perturbations in the lower stratosphere lead to higher values of λ (Joshi et al. 2003).

Global average radiative forcings in 2005 (best estimates with 5–95 % uncertainty ranges) with respect to 1750 for atmospheric constituents are +1.66 (range: +1.49 to +1.83) W m^{-2} for CO_2, +0.48 (+0.43 to +0.53) W m^{-2} for CH_4, +0.16 (+0.14 to +0.18) W m^{-2} for N_2O, +0.34 (+0.31 to +0.37) W m^{-2} for halocarbons, +0.35 (+0.25 to +0.65) W m^{-2} for tropospheric O_3, and +0.12 (+0.06 to +0.30) W m^{-2} for changes in solar irradiance (Fig. 1) (IPCC 2007a). On the other hand, anthropogenic contributions to aerosols (primarily sulphate aerosol, organic carbon, black carbon, nitrate and dust) produce an overall cooling effect, with a total direct radiative forcing of −0.5 (−0.9 to −0.1) W m^{-2} and an indirect cloud albedo forcing of −0.7 (−1.8 to −0.3) W m^{-2} (IPCC 2007a). The CO_2 radiative forcing increased by 20 % from 1995 to 2005, the largest change for any decade in at least the last 200 years (IPCC 2007a).

The global warming potential (GWP) is used within the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC) as a metric for weighting the climate impact of the emission of different greenhouse gases (IPCC 1990, 2001; Shine et al. 2005). The GWP is the time-integrated radiative forcing due to a pulse emission of a given gas, over some given time period (or horizon), relative to a pulse emission of carbon dioxide (IPCC 2001). GWPs are an index for estimating relative global warming contributions, due to the atmospheric emission of a kg of a particular greenhouse gas compared to the emission of a kg of carbon dioxide. For instance, CH_4 and N_2O have relatively long atmospheric residence times (12 and 114 years, respectively), which combined with their ability to efficiently absorb infrared radiation results into GWPs of 23 and 296 times, respectively, that of CO_2 on a per-kg basis and a 100 years time horizon (IPCC 2001). In addition, the perfluorocarbons (e.g. CF_4 and C_2F_6) and sulphur hexafluoride (SF_6) have really long atmospheric residence times (50000, 10000, and 3200 years, respectively) and are strong absorbers of infrared radiation. The resulting GWPs are 5700, 11900, and 22200 times, respectively, that of CO_2 on a per-kg basis for 100 years time horizon (Table 1) (IPCC 2001). Most of the halocarbons recently used (halogenated methanes and ethanes) show high GWPs ranging from 12 to 12000 times that of CO_2 on a per-kg basis for 100 years time horizon. Their atmospheric lifetimes vary from 0.3 to 260 years (Table 1) (IPCC 2001).

2.3 Key Issues that are Influenced by Global Warming

The key changes to the terrestrial and aquatic environments in response to global warming can be distinguished as: (i) increase of global average air and water temperatures (Fig. 2) (IPCC 2007a). Global surface temperatures have increased by 0.74 ºC since the late nineteenth century, and 11 out of the 12 warmest years on record have occurred since 1995 (IPCC 2007a).The temperature increase is widespread over the globe and is higher at higher northern latitudes. Indeed, average Arctic temperatures have increased at almost twice the global average rate in the past 100 years (IPCC 2007a). (ii) Decreases in snow cover and in the Northern Hemisphere sea ice extent. The result is a shorter freezing season for lakes, rivers and sea ice (Fig. 2) (IPCC 2007a). Since 1978, satellite data have been showing that the annual average Arctic sea ice extent has shrunk by 2.7 % (2.1–3.3 %) per

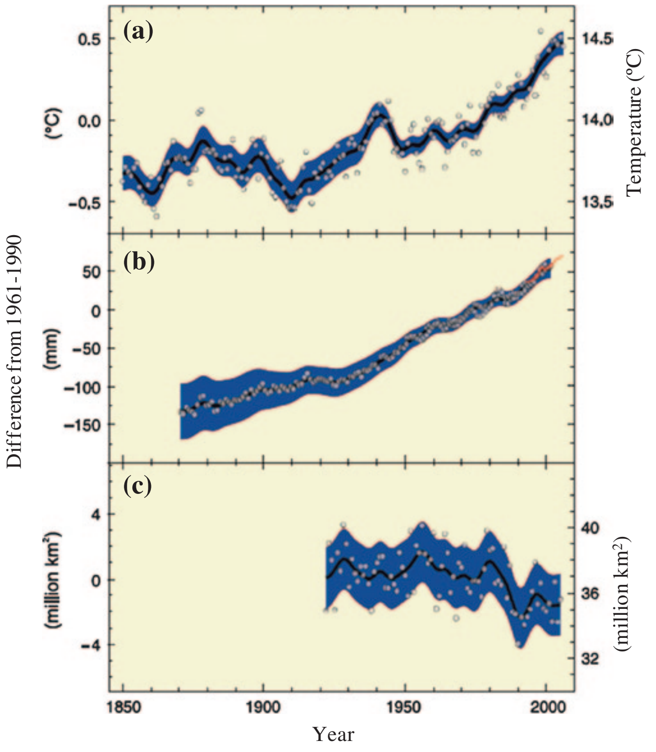


Fig. 2 Observed changes in **a** global average surface temperature; **b** global average sea level from tide gauge (*blue*) and satellite (*red*) data; and **c** Northern Hemisphere snow cover for March–April. All differences are relative to corresponding averages for the period 1961–1990. Smoothed curves represent decadal averaged values while circles show yearly values. The shaded areas are the uncertainty intervals estimated from a comprehensive analysis of known uncertainties (**a** and **b**) and from the time series (**c**). *Data source* IPCC (2007a)

decade, with summer decreases of 7.4 % (5.0–9.8 %) per decade (IPCC 2007a). The maximum surface of seasonally frozen ground has decreased by about 7 % in the Northern Hemisphere since 1900. There have been decreases in spring of up to 15 % (IPCC 2007a). (iii) Increase in soil temperature that subsequently enhances the soil respiration (Lloyd and Taylor 1994; Petersen and Klug 1994; Arnold et al. 1999; Feng and Simpson 2008, 2009; Frey et al. 2008). (iv) Weather modifications that can enhance natural disasters such as tornadoes, typhoons, storms, thunderstorms, and floods (Khalilov 2010). (v) Variations in water temperature profiles that cause changes in the euphotic zone, induce a longer summer stratification period and high photoinduced degradation of DOM and OM, make harmful algal blooms more likely, induce alteration of DOM dynamics, and change the seasonal patterns of chlorophyll or primary production and the nutrient concentrations. These effects induce as a consequence changes in species composition and in the seasonality of the water column, and finally modify food webs among phytoplankton, zooplankton, fish and birds in the aquatic environment (Huisman et al. 2006; Baulch et al. 2005; Castle and Rodgers 2009; Davis et al. 2009; Kitaysky and Golubova 2000; Hobson and McQuoid 2001; Mudie et al. 2002; Morrison et al. 2002; Johannessen and Macdonald 2009). (vi) Increases in sea level. They are consistent with warming and the global average sea level has risen at an average rate of 1.8 mm (1.3–2.3 mm) per year from 1961 to 2003. However, in the decade 1993–2003 the average rate has been of about 3.1 mm (2.4–3.8 mm) per year (IPCC 2007a). An increase of the global average temperature of about 2 ºC may cause a warming of about 2.7 ºC in the area around Greenland, possibly triggering the loss of the Greenland ice-sheet. Such a process may cause a global sea-level rise of 7 m over the next 1,000 years or more (Huybrechts et al. 1991; Gregory et al. 2004a, b). The rise of the sea level introduces vulnerability issues for agriculture, food, water resources, coral reefs, low-lying estuaries, intertidal zones, mudflats, mangrove forests, ecosystems and biodiversity (IPCC 2007a; Smith et al. 2001; Johannessen and Macdonald 2009; Doney et al. 2009; Masson and Cummins 2007; Burd et al. 2008a, b). The impacts on the coastal environments may lead to changes in the food web and affect the diversity of higher trophic levels such as marine mammals, fish and birds. (vii) A total ozone reduction of 2.5 % per decade during summer time causes a 5 % increase in UV irradiance (Varotsos and Kondratiev 1995), with a direct impact on terrestrial and aquatic environments.

3 Environmental Processes of GHGs Emission Affecting Global Warming

The key environmental processes of GHGs emission that may affect global warming can be categorized as follows: (i) soil respiration; (ii) agricultural activities in soil; (iii) anthropogenic sources of atmospheric greenhouse gases; (iv) deforestation; (v) photoinduced degradation of DOM and OM by natural sunlight; (vi) photoinduced degradation of OM in plants and soil environments.

3.1 Soil Respiration

In the soil respiration process, CO_2 fixed by terrestrial plants returns to the atmosphere.Changes in soil respiration in response to warming may contribute to the increase of CO_2 atmospheric levels (Bradford et al. 2008; Bahn et al. 2010; Feng et al. 2010; Raich and Schlesinger 1992; Oechel et al. 2000; Schlesinger and Andrews 2000; Luo et al. 2001; Melillo et al. 2002, 2004). CO_2 is produced in soils by roots, soil organisms and by chemical oxidation of carbon-containing materials (Lundegårdh 1927). Note that soil respiration through microbial activity can lead to the degradation to CO_2 of long chain ($>C_{20}$) alkanols, fatty acids (e.g. n-alkanoic acids), hydroxy fatty acids and di-acids that are major components of hydrolysable aliphatic lipids in soil organic matter (Feng et al. 2010; Nierop et al. 2003; Hajje and Jaffé 2006; Otto and Simpson 2006). These studies demonstrate that the average soil respiration rates are very variable depending on the nature of vegetation and on ambient temperature. For example, the lowest respiration rate is detected in tundra (60 ± 6 gC m^{-2} yr^{-1}), northern bogs and mires (94 ± 16 gC m^{-2} yr^{-1}), desert scrub (224 ± 38 gC m^{-2} yr^{-1}), boreal forests (322 ± 31 gC m^{-2} yr^{-1}) and marshes (413 ± 76 gC m^{-2} yr^{-1}). In contrast, respiration rates are highest in tropical moist forests (1260 ± 57 gC m^{-2} yr^{-1}), Mediterranean woodlands and heath (713 ± 88 gC m^{-2} yr^{-1}), temperate coniferous forests (681 ± 95 gC m^{-2} yr^{-1}), tropical dry forests (673 ± 134 gC m^{-2} yr^{-1}) and temperate deciduous forests (647 ± 51 gC m^{-2} yr^{-1}) (Raich and Schlesinger 1992). Temperature is the single best predictor of the annual respiration rate at a specific location, because soil respiration rates correlate significantly with average annual air temperatures and precipitation on a global scale (Raich and Schlesinger 1992).

Microbial decomposition of soil OM constituents such as lignin and hydrolysable lipids is promoted under both elevated CO_2 and N fertilization (Feng et al. 2010). Traditional tillage cultivation and rising temperature increase the flux of CO_2 from soils without increasing the stock of soil organic matter (Schlesinger and Andrews 2000). Soil warming can increase the relative abundance of Gram-positive bacteria (Frey et al. 2008; Bardgett et al. 1999; Biasi et al. 2005). It has also been shown that soil respiration is initially enhanced by warming for a few years, but that this effect is subsequently reduced over time (Frey et al. 2008; Oechel et al. 2000; Luo et al. 2001; Melillo et al. 2002, 2004). The following factors can be involved: (i) reduced plant production can lead to lower root respiration rates, decrease microbial activity because of soil drying, and to losses of labile soil organic carbon substrates such as amino acids, carbohydrates, and carboxylic acids (Frey et al. 2008; Oechel et al. 2000; Luo et al. 2001; Melillo et al. 2002). (ii) Increases in temperature can significantly change the microbial community structure that ultimately affects the soil respiration (Lloyd and Taylor 1994; Petersen and Klug 1994; Arnold et al. 1999; Feng and Simpson 2008, 2009; Frey et al. 2008).

Causes of diversity in respiration in the soil ecosystems are the variation in the decomposition factors of particulate detrital pools or vascular plant materials, which are regulated by numerous physical (temperature, moisture), chemical (redox, nutrient availability) and microbial (microfloral successional patterns, availability of microorganisms) factors (Mostofa et al. 2009a; Malcolm 1985; Wetzel 1992; Nakane et al. 1997; Uchida et al. 1998, 2000). Soil OM is typically lost upon agricultural conversion that reduces plant residue inputs, tillage-induced soil disturbance, erosion, and by the creation of more favorable conditions for microbial decomposition (Robertson and Grace 2004). The growth of typical terrestrial vegetation, rainforest, vascular plants and/or typical grassland and their degradation are significantly higher during the warm seasons than in the cold ones, because increased temperature would enhance respiration and decomposition in the soil environment (Nakane et al. 1997; Uchida et al. 1998, 2000; Duff et al. 1999; Fahey et al. 2005). The temperature increase is often found to enhance the soil CO_2 fluxes to the atmosphere (Fig. 3) (Feng and Simpson 2009).

However, the enhanced plant or litter inputs induced by warming have a stronger control on soil microbial responses than the temperature increase itself. Therefore, it is suggested that the quality of soil organic matter can control microbial responses to global warming (Feng and Simpson 2009; Rinnan et al. 2008; Zhang et al. 2005). The temperature effects outlined above may be comparatively less important at temperate latitudes, because the soil respiration rate is highly increased by temperature in areas where the soil temperatures are low (Lloyd and Taylor 1994; Biasi et al. 2005).

Warming might affect the abundance of soil microorganisms, but contrasting data are presently available. A 20–60 % increase in the fungal:bacterial ratio has been observed in a tallgrass prairie site, exposed to a ~2 ºC increase in temperature over a three-year period (Zhang et al. 2005), but another study has shown that the relative abundance of fungi was significantly reduced after 15 years of soil warming (1–2 ºC) in northern Sweden (Rinnan et al. 2008).

The global warming effect might be significantly different depending on the soil ecosystems. Indeed, changes in soil respiration and CO_2 fluxes are the effects of temperature and vegetation differences (Table 1) (IPCC 2001; Trumbore

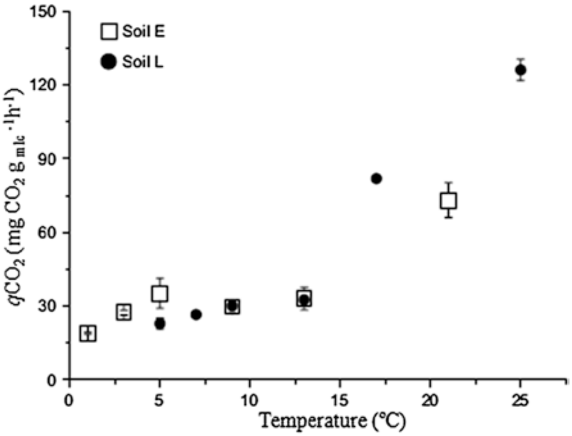


Fig. 3 Metabolic quotient (qCO_2) of both grassland soils on Day 1. Points show average values of triplicate (n = 3) and error bars represent standard error. Soil E and soil L are the two soil samples collected from the two different sites in Alberta, Canada. *Data source* Feng and Simpson (2009)

2000). Note that soil represents approximately 80 % of the carbon stocks in terrestrial ecosystems, ranging from 50 % in tropical forests to 95 % in tundra (IPCC 2002). The turnover times of OM, determined through ^{14}C tracer in well-drained boreal (Manitoba in Canada), temperate (central Massachusetts in the USA) and tropical forest soils (eastern Amazonia in Brazil), suggest that the average age of OM carbon is higher than the average age predicted from CO_2 production by OM decomposition (30, 8, and 3 yr for boreal, temperate, and tropical soil) or from total soil respiration (16, 3, and 1 yr, respectively) (Table 1) (IPCC 2001; Trumbore 2000). Most of the CO_2 produced during decomposition is derived from relatively short-lived soil organic matter (SOM) components. They do not represent a large fraction of the standing stock of soil organic matter (Trumbore 2000). Comparison of the ^{14}C in soil respiration with soil organic matter in temperate and boreal forest sites indicates a significant contribution from the decomposition of organic matter fixed >2 yr but <30 yr ago (Table 1) (IPCC 2001). Tropical soil respiration is dominated by C fixed <1 yr ago (Table 1) (IPCC 2001). Monitoring of the ^{14}C signature of CO_2 emitted from soils suggests that seasonal and interannual variability in soil respiration are the key factors in these ecosystems (IPCC 2001; Trumbore 2000) (Table 1).

These findings imply that the soil respiration is very variable in different ecosystems, with important effects on carbon sequestration and global carbon dynamics. It is estimated that on a global scale, the soil respiration in terrestrial ecosystems produces a CO_2 flux of approximately 75×10^{15} g C yr^{-1}, which is likely to increase due to changes in the Earth's condition (Schlesinger and Andrews 2000).

3.2 Agricultural Activities in Soil

The soil and the related agricultural activities can release significant amounts of CO_2, CH_4 and N_2O to the atmosphere (Mosier et al. 1989, 1991, 2004; Robertson and Grace 2004; Ambus and Robertson 2006; Smith et al. 2008; Kreileman and Bouwman 1994; IPCC 2001; Raich and Schlesinger 1992; Aselrnann and Crutzen 1989; Watson et al. 1992; Bowden et al. 1993; Subak et al. 1993; Zuidema et al. 1994; Freney 1997; Tsuruta et al. 1997; Stevens and Laughlin 1998; Cole et al. 1997; Tranvik et al. 2009). CO_2 is mostly released from agricultural activities and soil disturbances (IPCC 1996, 2007a; Subak et al. 1993; Bouwman 1990; Lal et al. 1999; Schlesinger 1999; Izaurralde et al. 2000). Several processes are responsible for the production of CO_2 from such activities: (i) CO_2 is produced during the processing, transport and application of N-containing fertilizers, which cause the release of around 1.4 mol of CO_2 per mole of N applied (Schlesinger 1999; Izaurralde et al. 2000; IPCC 1996). (ii) Land limes in the form of calcium carbonate ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] can produce bicarbonate and CO_2 (Robertson and Grace 2004; Liu et al. 2010, 2011). Note that $CaCO_3$ and $CaMg(CO_3)_2$ are commonly applied to agricultural soils to counteract soil acidity and to give supplies of Ca^{2+} and Mg^{2+} for plant uptake (Robertson and Grace 2004). $CaCO_3$ can react with soil Al^{3+} to form carbonic acid, raising the soil pH by the following reaction (Robertson and Grace 2004):

$$2Al^{3+} + 3CaCO_3 + 6H_2O \rightarrow 3Ca^{2+} + 2Al(OH)_3 + 3H_2CO_3 \quad (3.1)$$

Similarly, carbonic acid formed in the presence of CO_2 from root and microbial respiration reacts with solid carbonates [ca. $CaMg(CO_3)_2$] to produce bicarbonate by the following reaction (Eq. 3.2) (Robertson and Grace 2004):

$$CaMg(CO_3)_2 + 2\,H_2CO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4\,HCO_3{}^{-} \quad (3.2)$$

A strong mineral acid such as nitric acid (HNO_3) can react with carbonates [e.g. $CaMg(CO_3)_2$] to produce CO_2 by the following reaction (Robertson and Grace 2004):

$$CaMg(CO_3)_2 + 4\,HNO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4\,NO_3{}^{-} + 2\,CO_2 + 2\,H_2O \quad (3.3)$$

Nitric acid is formed by nitrifying bacteria in most soils, including acid tropical soils (Robertson 1982; Sollins et al. 1988).

(iii) Calcium-saturated groundwater can react with soil $HCO_3{}^{-}$ to produce CO_2 by the following reaction (Robertson and Grace 2004; Schlesinger 1999):

$$Ca^{2+} + 2\,HCO_3{}^{-} \rightarrow CaCO_3 + H_2O + CO_2 \quad (3.4)$$

Carbonate reactions also occur when calcium-saturated groundwater is sprayed on calcareous surface soils (Schlesinger 1999). In arid regions groundwater often contains as much as 1 % Ca and CO_2 (Robertson and Grace 2004).

CH_4 has a microbial origin from natural (e.g. wetlands) and human-influencewd sources, such as agricultural activities (rice and crops cultivation), enteric fermentation, animal wastes and landfills (Mosier et al. 1991, 1998, 2004; Robertson and Grace 2004; Smith et al. 2008; IPCC 2001; Watson et al. 1992; Subak et al. 1993; Zuidema et al. 1994; Crutzen et al. 1986; Bingemer and Crutzen 1987; Cicerone and Oremiand 1988; Robertson et al. 2000). Methane is produced when organic materials are decomposed in oxygen-deprived conditions, including fermentative digestion by ruminant livestock, stored manures and rice grown under flooding (Mosier et al. 1998). A recent study estimates that agriculture accounts for 52 % of the global anthropogenic CH_4 emissions (Smith et al. 2008).

N_2O emission by agricultural activities in soil is accounted for by microbial nitrification, denitrification and chemo-denitrification, especially under wet conditions. N_2O is also produced by the microbial transformation of nitrogen in soil and manure (IPCC 2007a; Robertson and Grace 2004; Smith et al. 2008; Kreileman and Bouwman 1994; Mosier et al. 1989, 1991; Freney 1997; Tsuruta et al. 1997; Stevens and Laughlin 1998; Robertson et al. 2000; Cavigelli and Robertson 2000; Xing et al. 2002; Mahimairaja et al. 1994; Smith and Conen 2004; Oenema et al. 2005). Natural sources of N_2O have been estimated to be approximately 10 TgN/yr in 1990. Soils account for about 65 % of the sources, oceans for about 30 % (IPCC 2001). It is estimated that agriculture accounts for 84 % of the global anthropogenic N_2O emissions (Smith et al. 2008).

3.3 Anthropogenic Sources of Atmospheric GHGs

Anthropogenic sources are primarily responsible for the greenhouse gases (GHGs) inputs to the atmosphere. CO_2 is mostly produced anthropogenically from the burning of fossil fuels and plant litter and from oil flaring, cement manufacturing and other industrial activities (IPCC 2007a; Sabine et al. 2004; Smith 2004; Archer 2005; Canadell et al. 2007; Hofmann et al. 2009; Subak et al. 1993; Marland and Rotty 1984; Crutzen and Andreae 1990; Keeling et al. 1996). It has recently been shown that the annual emissions because of fossil fuel burning have grown by about 80 %, from 21 to 38 gigatonnes (Gt), between 1970 and 2004. The rate of growth of CO_2-eq emissions was much higher during the more recent decade 1995–2004 (0.92 GtCO_2-eq per year) than during the previous period 1970–1994 (0.43 GtCO_2-eq per year) (IPCC 2007a). CH_4 is produced from fossil fuel production and consumption including oil and gas field activities, coal mining, plant litter/wood processing, domestic sewage treatment, enteric fermentation and other biomass burning (Mosier et al. 2004; Smith 2004; Kreileman and Bouwman 1994; IPCC 2001; Subak et al. 1993; Crutzen 1991; Flessa et al. 2002). The major sources of anthropogenic aerosols are sulfur-containing fossil fuels, biomass burning and explosive volcanic eruptions (IPCC 2001, 2007a).

3.4 Deforestation

Deforestation or changes in land-surface cover can significantly affect atmospheric CO_2, CH_4 and N_2O (IPCC 2001, 2007a; Kreileman and Bouwman 1994; van der Werf et al. 2009; Raich and Schlesinger 1992; Subak et al. 1993; Bouwman 1990; Crutzen and Andreae 1990; Keller et al. 1986; Sitch et al. 2005; Detwiler and Hall 1988; Myers 1989; Houghton 1991). The above-cited processes can contribute in three ways to global warming: First, deforestation i.e. the decline of terrestrial plants can significantly reduce the uptake of CO_2 from the atmosphere by photosynthesis, which is vital for plants growth. Such a phenomenon would thus give indirect contribution to the increase of atmospheric CO_2. Second, deforestation can reduce evaporation and increases surface temperature. Third, changes in land-surface cover can enhance the degradation of soil DOM and OM by both photoinduced and microbial processes, thus uncovered land surfaces can release GHGs directly to atmosphere (Schiettecatte et al. 2006, 2007; Borges et al. 2008; Omar et al. 2010; Brandt et al. 2009; Rutledge et al. 2010; Thomas et al. 2004, 2005, 2007; Raich and Schlesinger 1992; Xie et al. 2004). Soil respiration rates are very high in the first year after the clear-cutting of plants, apparently due to the higher soil temperatures and to the decomposition of the debris that the soil incorporated during the deforestation (Raich and Schlesinger 1992). Deforestation is the second largest anthropogenic source of CO_2 to the atmosphere after fossil fuel burning. It accounted for 17.3 % of anthropogenic GHGs in the 2004 total emissions to the atmosphere (IPCC 2007a; van der Werf et al. 2009). Large-scale deforestation in the humid tropics has been identified as the main, ongoing land-surface process caused by industrialization and by growing agricultural activities because of the increasing demands of a growing population.

3.5 Photoinduced and Microbial Degradation of Organic Matter (OM) in Natural Waters

The production of CO_2 and of other dissolved inorganic carbon (DIC: generally defined as dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}) species upon photoinduced and microbial degradation of organic matter including DOM and POM (e.g. algae or phytoplankton) can potentially influence the carbon cycling and may have an impact on climate change (Bozec et al. 2005, 2006; Schiettecatte et al. 2006, 2007; Borges et al. 2008; Omar et al. 2010; Ballaré et al. 2011; Zepp et al. 2011; Kelley 1970; Kempe and Pegler 1991; Hoppema 1990, 1991; Borges and Frankignoulle 1999, 2002a, b; Brasse et al. 1999; Frankignoulle and Borges 2001; Thomas et al. 2004, 2005, 2007; Tranvik et al. 2009; Xie et al. 2004; Salonen and Vähätalo 1994; Granéli et al. 1998; Richey et al. 2002; Clark et al. 2004; Kujawinski et al. 2009; Koprivnjak et al. 2010). The waterbed in subtropical and tropical latitudes generally acts as a CO_2 source to the atmosphere, while at high and temperate latitudes it rather acts as a CO_2 sink by uptake from the atmosphere (Omar et al. 2010; Borges and Frankignoulle 2002a; Thomas et al. 2004; Sobek et al. 2005; Gattuso et al. 1993, 1997; Frankignoulle et al. 1996, 1998; Goyet et al. 1998; Tsunogai et al. 1999; Yool and Fasham 2000; Bates et al. 2001; Cai et al. 2003, 2006; Borges 2005; Ito et al. 2005; Ohde and van Woesik 1999; Wang and Cai 2004; Chen and Borges 2009; Wang et al. 2011). In temperate regions, increased temperatures and longer residence times of OM in water, which might be caused by decreased runoff could accelerate microbial respiration and photoinduced degradation of organic carbon. However, the combined effects of increased autochthonous production and increased organic carbon burial efficiency due to increased anoxia may offset increased CO_2 production (Tranvik et al. 2009). It should also be considered that increases in production, duration of stratification and sedimentation may favor the occurrence of hypolimnetic anoxia and, as a consequence, CH_4 production in temperate zones (Tranvik et al. 2009). Larger emissions of CO_2 and CH_4 may occur in Arctic regions, particularly where thermokarst erosion and ponding is occurring (Walter et al. 2006). Moreover some boreal streams, some major rivers, lakes in general or boreal lakes in particular are supersaturated in CO_2 and are considered to be net sources of CO_2 to the atmosphere (Fahey et al. 2005; Koprivnjak et al. 2010; Sobek et al. 2005; Jones and Mulholland 1998; Dawson et al. 2001; Hope et al. 2001; Finlay 2003; Öquist et al. 2009; Teodoru et al. 2009; Cole and Caraco 2001; Jones et al. 2003c; Yao et al. 2007; Huttunen et al. 2003a).

The air–sea CO_2 exchange occurs mostly in temperate regions (Borges and Frankignoulle 2002a, b; Borges 2005; Andersson et al. 2003; Andersson and Mackenzie 2004; Zhai et al. 2005). However, waters in upwelling regions act both as sinks (California and Oman coasts) and as sources (Galician and Oregon coasts) of atmospheric CO_2 (Borges and Frankignoulle 2002a, b; Goyet et al. 1998; Friederich et al. 2002; Hales et al. 2005). The global coastal zone is still a net source of CO_2 to the atmosphere, due to the combination of calcification and of net heterotrophy that is a feature of estuarine ecosystems (Frankignoulle et al. 1998; Borges 2005; Cai and Wang 1998; Raymond et al. 2000; Sarma et al. 2001; Mukhopadhyay et al. 2002; Bouillon et al. 2003; Abril et al. 2003, 2004; Mackenzie et al. 2004; Fagan and Mackenzie 2007). Indeed, when estuaries are included in the CO_2 exchange budget, the global shallow-water coastal ocean is a net source of CO_2 to the atmosphere (Borges 2005).

The production of CO_2 and its input to the atmosphere is considerably higher during the summer and fall (or dry) seasons than in winter and spring (or wet) seasons. In the latter case the waterbed actually acts as a net sink for atmospheric CO_2. The reason behind this phenomenon is that the photoinduced and microbial degradation of DOM and POM are greatly enhanced in surface waters during the summer period due to high solar radiation and longer summer day-time. CO_2 emission by boreal streams is quite high during summer and very low in spring, which might be a consequence of photoinduced processing of DOM and POM (Koprivnjak et al. 2010). Obviously, the solar intensity is significantly reduced during the winter season that also has shorter day-time. In addition, estuaries often have high contents of DOM that undergoes strong photoinduced degradation and makes these systems to be significant sources of CO_2 to the atmosphere. The concentration of dissolved organic carbon (DOC) explains the significant variation of lake pCO_2 (Sobek et al. 2005), which might be an effect of photoinduced and microbial release of CO_2 from DOM and POM in water as mentioned before. Supersaturation of CO_2 in freshwater ecosystems (streams, rivers and lakes) is possibly caused by the same photoinduced and microbial processes that degrade DOM and POM. Indeed, freshwater ecosystems generally contain high amounts of DOM and POM that are potentially important microbial or photoinduced sources of CO_2 or DIC.

The situation is much different at northern latitudes: it is estimated that the direct photo-oxidation of organic carbon to CO_2 accounted for less than 10 % of dark respiration in the epilimnion of six boreal lakes (Granéli et al. 1996). CO_2 emission is also mainly derived from in-lake respiration in the lake environments (del Giorgio et al. 1999; Jansson et al. 2000). Anyway, global warming will increase the atmospheric temperature that can enhance both the photoinduced and the microbial degradation of DOM and POM, during all seasons and at all latitudes. The consequence would obviously be a further increase of atmospheric CO_2. Warming is also expected to reduce terrestrial and ocean uptake of atmospheric CO_2, increasing the fraction of anthropogenic emissions that remain in the atmosphere. This would result into an additional increase of atmospheric CO_2 (IPCC 2007a).

A positive correlation of $p\text{CO}_2$ levels with CDOM and chlorophyll has been observed in the Southwest Florida Shelf, indicating that CO_2 may be produced from the photoinduced degradation of CDOM in natural waters (mostly in the dry season), from microbial respiration and from shifts in the carbonate equilibrium (Clark et al. 2004). The effect is a release of CO_2 into the atmosphere from DOM that has been formed by primary production (Thomas et al. 2009). On the other hand, microbial degradation of DOM and OM in natural waters and sediment pore waters can release CH_4 to the atmosphere (Mosier et al. 2004; Cicerone and Oremiand 1988; Pepper et al. 1992; Bastviken et al. 2004, 2008; Bergström et al. 2007). Anoxia in freshwater sediments contributes to high CH_4 emissions, and the production of CH_4 in epilimnetic sediments is the main driver of methane emission from surface waters (Bastviken et al. 2004, 2008). Methane production can also be enhanced by water temperature and lake level fluctuations. Such effects can affect carbon balances depending on the predominant plant species and sediment properties (Bergström et al. 2007). It is estimated that the contribution of CH_4 to the atmosphere is 100–200 Tg yr^{-1} from wetlands, 5–20 Tg yr^{-1} from oceans, and 1–25 Tg yr^{-1} from freshwater (Mosier et al. 2004). N_2O can be released from freshwater and oceanic environments (Watson et al. 1992; Seitzinger 1990). Increases in oxygen-deficient regions in the ocean caused by climate changecould enhance the emissions of nitrous oxide, an important greenhouse and ozone-depleting gas (Zepp et al. 2011).

The upper ocean microbial food web (mostly the autotrophs) is a huge carbon-processing machine that can remove CO_2 from the atmosphere, but part of the carbon fixed by autotrophy is actually respired in situ (Sarmento et al. 2010). The heterotrophic bacteria are responsible for the major respiration (>95 %) in the ocean (del Giorgo and Duarte 2002), and half of it (approximately 37 Gt of C per year) takes place in the euphotic layer (del Giorgio and Williams 2005). Notes that global ocean respiration is approximately as important as the oceanic primary production (del Giorgo and Duarte 2002; Karl et al. 2003; Williams PJlB et al. 2004; Riser and Johnson 2008). Increasing temperature will often increase respiration rates in natural waters (Vázquez-Domínguez et al. 2007). Increasing aquatic respiration is presumably the result of enhanced photo- and microbial products (H_2O_2, CO_2, DIC, etc.) derived from the photoinduced and microbial degradation of DOM and OM in the euphotic zone. The temperature increase accelerates the respiratory consumption of organic carbon relative to the autotrophic production, with a decrease in the biological drawdown of DIC. A decrease of up to 31 % has been observed in mesocosms warmed by 2, 4 and 6 ºC (Wohlers et al. 2009). Changes in the biogenic carbon flow induced by warming have the potential to reduce the transfer of primary produced OM to higher trophic levels (Vázquez-Domínguez et al. 2007; Wohlers et al. 2009; Laws et al. 2000). This would weaken the ocean's biological carbon pump and provide a positive feedback to the rise of atmospheric CO_2 (Vázquez-Domínguez et al. 2007; Wohlers et al. 2009; Laws et al. 2000).

The photoinduced and microbial activities of DOM and POM in natural surface waters may act as sources or sinks of N_2O that is produced via nitrification and denitrification (Tranvik et al. 2009; Mengis et al. 1997; Huttunen et al. 2003b, 2004; Wang et al. 2006). N_2O may be consumed in the hypolimnion, whilst shallow sediments contribute to N_2O emissions to the atmosphere (Huttunen et al. 2003b; Wang et al. 2006).

3.6 *Photoinduced and Microbial Degradation of OM in Plants and Soil Environments*

Photoinduced and microbial processes can directly degrade the organic matter (OM) in terrestrial plants and in soil environments, releasing CO_2 to the atmosphere (Brandt et al. 2009; Rutledge et al. 2010). Photodegradation contributes 19 % of the annual CO_2 flux from peatland and almost 60 % of the dry-season CO_2 flux from grassland. The respective fractions of the summer mid-day CO_2 fluxes are up to 62 and 92 % (Rutledge et al. 2010). Photodegradation may be important in a wide range of ecosystems with exposed OM (Rutledge et al. 2010). Plant litter can be exposed outdoors to natural solar radiation. It has been shown that in clear sunny days, close to the summer solstice at mid-latitude, UV radiation (280–400 nm) accounted for 55 % of the photolytically induced CO_2 production, while shortwave visible radiation (400–500 nm) accounted for the remaining 45 % (Brandt et al. 2009). Abiotic mineralization to CO_2 is the primary mechanism by which C is lost from litter during photodegradation. It is estimated that annual CO_2 production via photodegradation could be between 1 and 4 g C m^{-2} a^{-1} in arid ecosystems in the southwestern United States (Brandt et al. 2009).

4 Impacts of Global Warming on Natural Waters

Global warming may severely affect various physical, chemical and biological processes that involve DOM in natural waters. The main effects are the following: (i) Changes in the light cycle and increase of water temperature; (ii) Increase of the photoinduced activity of natural waters; (iii) Changes in the microbial activity in natural water; (iv) Changes in photosynthetic processes in natural waters; (v) Changes in the primary production and disorders in the chlorophyll *a* maxima; (vii) Changes in the DOM dynamics and in the global carbon cycle. (viii) Changes in the nutrients cycle.

4.1 *Changes in the Light Cycle and Increase of Water Temperature*

Global warming could cause changes in the seasonal light cycle and an increase in water temperature, which affects the light distribution in the euphotic zone

(Rutledge et al. 2010; O'Reilly et al. 2003; Letelier et al. 2004; Porcal et al. 2009; Morrison et al. 2002; Ryther 1956). Notes that the depth of the euphotic zone is defined as the depth where the photon flux density equals 1 % of that measured at the air–sea interface (Ryther 1956). The temperature increase is a global effect, but it is higher northern latitudes. Average Arctic temperatures have in fact increased at almost twice the global average rate in the past 100 years (IPCC 2007a). Temperatures at the top of the permafrost layer have generally increased in the Arctic by up to 3 °C since the 1980s (IPCC 2007a). The global average surface air temperature has increased by 0.74 °C over the past century and is projected to rise by another 1.1 to 6.4 °C before 2100. The sea level could increase by 0.2 to 0.6 m or more before 2100 (Hansen and Sato 2004; IPCC 2007b). The long-term observations in European seas show that the increase of the sea-surface temperature rate is around 0.01 ºC yr^{-1} since the 1860s (Wiltshire and Manly 2004; Vargas-Yañez et al. 2005; Mackensie and Schiedek 2007). The combination of temperature increase and of the decrease in water flow allow the prediction of a 10-fold increase, by the end of this century, of the number of days when the temperature of the Fraser River exceeds 20 °C. Such a phenomenon may threaten the survival of some specific fish and other aquatic microorganisms (Morrison et al. 2002). Global warming may expand the summer season and increase the water column transparency as well as the water temperature, which might accelerate the photoinduced degradation of DOM through e.g. an enhanced production of $HO^{\bullet}$ (Huisman et al. 2006; Zellner et al. 1990; Malkin et al. 2008). At the same time, there can be an increase of UV radiation during ozone hole events (Huisman et al. 2006; Kerr and McElroy 1993; Varotsos and Kondratiev 1995; Qian et al. 2001; Sarmiento et al. 2004; Schmittner 2005). Previous studies show that the incident UV-B radiation has increased at a rate of 10–20 % per decade at temperate latitudes (Kerr and McElroy 1993), and a total ozone reduction of 2.5 % per decade during summer would cause a 5 % increase in the UV irradiance (Varotsos and Kondratiev 1995).

Although the increase of the chlorine concentration in the stratosphere has slowed down, reflecting the execution of the Montreal Protocol, the time required for the recovery of the ozone layer is unconvincing and will rely on the impacts of the climate change on the stratosphere (Weatherhead and Andersen 2006). The global warming phenomenon is expected to enhance the temperature in the troposphere, but at the same time there will be cooling effects in the stratosphere that can enhance ozone depletion. An increase of UV-B radiation may greatly enhance the production of $HO^{\bullet}$ due to an increase in direct photolysis rates of NO_2^-, NO_3^- and Chromophoric Dissolved Organic Matter (CDOM), and also other redox reactions may be enhanced, in particular in the Antarctic and Arctic regions (Qian et al. 2001; Randall and Harvey 2005). The $HO^{\bullet}$ formation from nitrate, nitrite and CDOM significantly increases during ozone hole conditions (Qian et al. 2001). Two effects may derive from this scenario. First, ozone hole conditions may enhance the photoinduced degradation of aquatic DOM, which can subsequently release a large amount of CO_2 to atmosphere. Second, high production of $HO^{\bullet}$ can reduce the biological activity through oxidative damages to the living cells of biota in the aquatic environments (Berlett and Stadtman 1997; Paradies et al. 2000;

Blokhina et al. 2003). Ocean warming and acidification due to increased atmospheric CO_2 concentration may exacerbate the detrimental effects of solar UV-B radiation (Häder 2011). Finally, exposure to solar UV radiation can reduce productivity, affect reproduction and development, and increase the mutation rate in phytoplankton, macroalgae, eggs, and larval stages of fish and other aquatic animals (Häder et al. 2007). Consequences of decreased productivity are a reduced sink capacity for atmospheric carbon dioxide and negative effects on species diversity, ecosystem stability, trophic interactions and ultimately global biogeochemical cycles (Zepp et al. 2007).

Since 1993 the thermal expansion of the oceans has contributed about 57 % of the overall sea level rise, while decreases in glaciers and ice caps contributed about 28 % and the remainder was accounted for by losses from the polar ice sheets (IPCC 2007a).

4.2 *Increase of Photoinduced Activity in Natural Waters*

Global warming causes an increase in water temperature that can accelerate the photoinduced activity of DOM and of other chemical constituents in surface waters. Photoinduced degradation of DOM and OM can produce a number of photo-products including H_2O_2 and DIC (dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}) (Molot et al. 2005; Johannessen et al. 2007; Mostofa and Sakugawa 2009; Mostofa et al. 2009a, b, 2011; Xie et al. 2004; Clark et al. 2004; Miller and Zepp 1995; Thomas and Lara 1995; Dillon and Molot 1997; Miller 1998; Gennings et al. 2001; Johannessen and Miller 2001; Rochelle-Newall and Fisher 2002; Ma and Green 2004; Hiriart-Baer and Smith 2005). Autochthonous DOM can be released in natural waters by algae or phytoplankton upon photoinduced degradation or photorespiration (Mostofa et al. 2009a, b; Stedmon et al. 2007a, b; Thomas and Lara 1995; Rochelle-Newall and Fisher 2002; Fu et al. 2010), and it has recently been shown that the algal-derived CDOM is a more efficient photoinduced substrate than terrigenous material (Johannessen et al. 2007). In situ incubation of natural phytoplankton assemblages in Antarctic waters indicates that, under normal ozone conditions, UV-B radiation is responsible for a loss of approximately 4.9 % of the primary production in the euphotic zone. UV radiation with wavelengths between 320 and 360 nm causes a loss of approximately 6.2 % (Holm-Hansen et al. 1993a). Ambient levels of UV radiation (280–400 nm) are observed to decrease substantially the rates of carbon fixation by phytoplankton (Holm-Hansen et al. 1993a; Karentz et al. 1991; Cullen et al. 1992; Helbling et al. 1992; Smith et al. 1992; Li et al. 2011), and photoinduced release of DOM from phytoplankton can also take place. UV-B radiation accelerates the decomposition of colored DOM entering the sea via terrestrial runoff, thus having important effects on the oceanic carbon cycle (Zepp et al. 2003).

The increase of water temperature significantly enhances the efficiency of the Fenton and photo-Fenton reactions, as well as the photolysis of NO_2^-, NO_3^- and

H_2O_2. All these compounds are responsible for the production of $HO^\bullet$ towards the degradation of DOM or organic pollutants in aqueous solution (Zellner et al. 1990; Zafiriou and Bonneau 1987; Millero and Sotolongo 1989; Zepp et al. 1992; Farias et al. 2007). It is estimated from data of Zellner et al. (Zellner et al. 1990) that a temperature increase from 278 to 298 K can enhance the quantum yield of $HO^\bullet$ photoproduction (at 308 nm and at neutral pH), on average by 70 % for NO_2^- photolysis, 129 % for NO_3^- photolysis and 20 % for H_2O_2 photolysis. The efficiency of the photoinduced degradation of DOM is also significantly dependent on the wavelength, and the quantum yields (Φ_{HO}) of $HO^\bullet$ production decrease with increasing wavelength (Zellner et al. 1990; Zafiriou and Bonneau 1987). At pH 8 and at 298 K the Φ_{HO} for NO_2^- photolysis at 308 nm is on average 54 % higher ($\Phi_{HO} = 0.071 \pm 0.009$) than that at 351 nm ($\Phi_{HO} = 0.046 \pm 0.003$) (Zellner et al. 1990).

The formation of H_2O_2 is a key step of the photoinduced processes in surface waters (Mostofa et al. 2011) and it is as well largely dependent on the radiation wavelengths (Obernosterer et al. 2001; Richard et al. 2007). The contribution of UV-B, UV-A and photosynthetically active radiation (PAR) to H_2O_2 formation is 40, 33 and 27 %, respectively (Richard et al. 2007).

An increase in the photoinduced degradation rate of DOM may extend the water column transparency (which undergoes seasonal modifications on a variety of time scales) and the depth of the mixed layer that influences the incident UV radiation (Scully and Lean 1994; Morris et al. 1995; Morris and Hargreaves 1997). Diffuse light attenuation coefficients often undergo seasonal variations (39–81 %) in surface waters, and minimum values appear during the summer season (Morris and Hargreaves 1997). Therefore, an extension of the summer season due to global warming may enhance both photoinduced processes and photosynthesis, which could for instance increase the duration of the phytoplankton or algae productivity in lake ecosystems, particularly in the Arctic and Antarctic regions (Malkin et al. 2008). As already indicated, an increase in UV radiation due to depletion of the stratospheric ozone layer can accelerate the production of $HO^\bullet$, which is a key factor for the photoinduced degradation of DOM in natural waters (Huisman et al. 2006; Qian et al. 2001; Sarmiento et al. 2004; Schmittner 2005; Crutzen 1992; Stolarski et al. 1992). Therefore, global warming can enhance both the photoinduced degradation of DOM and the release of autochthonous DOM and nutrients from algae or phytoplankton. Such processes can be partially offset by the fact that the production of higher amounts of H_2O_2, CO_2, DIC and other low molecular weight substances could increase photosynthesis and enhance the primary production (Mostofa et al. 2009b).

4.3 Changes in Microbial Activity in Natural Waters

Global warming may significantly affect microbial or biological processes in natural waters, with consequences on both autotrophs (plants, algae, bacteria) and heterotrophs (animals, fungi, bacteria). An increase of temperature can change (or enhance) microbial activities including bacterial production, respiration, photosynthesis and growth efficiency, as well as bacterial–grazer trophic interactions, which can result in the rapid mineralization of organic matter in natural waters, particularly in Arctic and Antarctic ecosystems (Norf et al. 2007; Vázquez-Domínguez et al. 2007; Falkowski and Oliver 2007, 2008; Peters 2008; Norf and Weitere 2010; Sarmento et al. 2010; Sawicka et al. 2010; Nedwell and Rutter 1994; Ochs et al. 1995; Felip et al. 1996; Nedwell 1999; Reay et al. 1999; Vrede 2005; Morán et al. 2006; López-Urrutia and Morán 2007). These studies show that an increase in temperature may enhance the availability of labile substrates, which is responsible for an increase of microbial activity at elevated temperature.

The response to temperature of a species or microorganism is characterized by a number of 'cardinal temperatures': upper and lower limits of temperature for growth, and an optimum growth temperature included between the two extremes (Morita 1975). Microorganisms living near the lower temperature limit of a species can be stimulated either by higher temperature or by higher concentrations of added substrates in natural waters (Pomeroy et al. 1991; Wiebe et al. 1992, 1993). The microbial metabolism modifies organic nutrients such as glucose and the functional groups of macromolecules such as fulvic and humic acids of vascular plant origin or autochthonous fulvic acids of algal origin. The consequence of microbial processing may be the release in water of a variety of end products such as H_2O_2, CO_2, DIC, PO_4^{3-}, NH_4^+ and CH_4 (Mostofa and Sakugawa 2009; Ma and Green 2004; Fu et al. 2010; Palenik and Morel 1988; Lovley et al. 1996; Zhang et al. 2004, 2009; Kim et al. 2006; Li et al. 2008). Algae or phytoplankton biomass can release autochthonous DOM by microbial degradation or assimilation (Mostofa et al. 2009a, b, 2011; Stedmon et al. 2007a, b; Rochelle-Newall and Fisher 2002; Fu et al. 2010; Zhang et al. 2009; Biddanda and Benner 1997; Yamashita and Tanoue 2004, 2008; Stedmon and Markager 2005), and an increase in temperature can accelerate the bacterial degradation of phytoplankton-derived organic matter (Wohlers et al. 2009; Hoppe et al. 2008). Small algae carry out 40–95 % of total grazing on bacteria in the euphotic layer of the temperate North Atlantic Ocean in summer (Zubkov and Tarran 2008). A similar range (37–70 %) has been observed in the surface waters of the tropical Northeast Atlantic Ocean (Zubkov and Tarran 2008).

In Lake La Caldera it has been observed that at the lower temperature values (5.0–7.0 ºC) one finds higher bacterial abundance ($3.9–7.9 \times 10^5$ cells ml^{-1}, mean = 6.4) and higher bacterial biomass (4.0–6.7 μg C L^{-1}, mean = 5.2) compared to the higher temperature values (7.5–11.1 ºC), which yielded $1.3–2.5 \times 10^5$ cells ml^{-1} (mean = 1.8) and 1.3–2.4 μg C L^{-1} (mean = 1.7) for bacterial abundance and biomass, respectively (Carrillo et al. 2002). The grazing on bacteria increases with increasing temperature, but the rate of the increase is maximum at temperatures lower than 2 ºC, whilst bacterial production increases at higher rates at temperatures higher than 2 ºC. Such a finding, obtained in a microcosm experiment with temperature manipulation (-1 to 5 ºC) of Antarctic waters, suggests that bacterial production and bacterial grazing could become uncoupled processes at higher temperatures (Vaqué et al. 2009). Polar oceans at temperatures of −1 to 2−3 °C have microbial communities, both bacterial and algal, which are physiologically stressed. In fact, the environmental temperature is well below the optimum temperature for growth of many inhabitants (Nedwell 1999). As average Arctic temperatures have increased at almost twice the global average rate in the past 100 years (IPCC 2007a), the microbial activity in the Arctic and Antarctic regions is expected to undergo a significant enhancement due to the effect of global warming.

Winter warming typically results in both stimulation (abundance and biomass) of the biofilm ciliate communities and in significant shifts in the community structure. Summer warming induces a significant decline in the ciliate biomass but does not affect the relative community composition (Norf and Weitere 2010). Gradual freeze–thaw incubation decreases the microbial activity in the frozen state to 0.25 % of the initial levels at 4 °C, but activity resumes rapidly reaching >60 % of the initial activity in the thawed state (Sawicka et al. 2010).

Uptake of nitrate by bacteria and algae is strongly dependent on temperature and consistently decreases at temperatures below the optimum. In contrast, ammonium uptake is increased at low temperatures (Reay et al. 1999). Increasing temperature can significantly accelerate the colonization speed and reduce the carrying capacity in particular seasons, e.g. during winter. At the same time, the strongest response to the temperature increase occurs during the highest DOC loadings (Norf et al. 2007). Overall, the response of microbial communities to local temperature increases strongly depends on the seasonal setting, the resource availability and the stage of succession (Norf et al. 2007).

Bacterioplankton production depends on ambient temperature, availability of nutrients and other labile substrates, and on the total DOM contents in natural waters (Ochs et al. 1995; Felip et al. 1996; Vrede 1996, 2005; Morris and Lewis 1992; Wang et al. 1992; Coveney and Wetzel 1995; Elser et al. 1995; Cotner et al. 1997; Simon and Wünsch 1998; Caron et al. 2000; Pomeroy and Wiebe 2001; Vrede et al. 1999). Bacteria in temperate lakes are temperature-dependent up to a certain threshold value, above which other factors regulate their growth (Ochs et al. 1995; Felip et al. 1996). In the mesotrophic Lake Constance it has been found that during most of the year the bacterial community is well adapted to in situ temperatures (ranging from 4 to 23 °C) in the upper water column, whilst in the deeper strata the bacterial growth is limited by temperature (ranging between 4 and 10 °C) (Simon and Wünsch 1998). The growth of bacteria that live at low temperatures is stimulated both by increases in temperature and by addition of organic substrates (Pomeroy et al. 1991). Bacterioplankton growth can be limited by inorganic nutrients, by phosphorus (P) and by organic carbon (C), and the limitation effect is observed either for each constituent alone or for variable constituent combinations in both freshwater and marine systems (Vrede 1996, 2005; Morris and Lewis 1992; Wang et al. 1992; Elser et al. 1995; Cotner et al. 1997; Caron et al. 2000; Vrede et al. 1999). Substrate concentrations and temperature intergo very close interactions, and the interactive effects can vary with the temperature regime (Pomeroy and Wiebe 2001). It has been shown that increased temperature can stimulate bacterioplankton production when the in situ temperatures are low, i.e., in the hypolimnion in summer and in the mixed water column in autumn (Vrede 2005). At low temperatures, both the temperature increase and the addition of P (in the hypolimnion in summer) or C (in autumn) had strong effects on bacterioplankton production (Vrede 2005). The interaction between P and temperature is only significant in the epilimnion in summer. At the same time, temperature alone had no effect whilst P alone had a strong effect on bacterioplankton production (Vrede 2005). It is hypothesized that high temperature can accelerate the photoinduced and microbial release of nutrients, labile organic substrates and other products (e.g. H_2O_2, CO_2 and DIC) from algae, phytoplankton or DOM. Such processes take place in both the epilimnion and the hypolimnion and are susceptible to enhance the bacterioplankton production in natural waters.

4.4 Changes in Photosynthetic Processes in Natural Waters

Phytoplankton cells within the euphotic zone utilize photosynthetically active radiation (PAR, 400–700 nm) to drive photosynthesis; at the same time, they are exposed to UV radiation (UVR, 280–400 nm) that can penetrate up to 60 m into the pelagic water column (Smith and Baker 1979). Short-term UV-B exposure can severely inhibit the photosynthetic capability, which can be restored quickly after transfer to low PAR conditions (Jiang and Qiu 2011). Solar UV-A radiation can act as an additional source of energy for the photosynthesis carried out by coastal marine phytoplankton assemblages in tropical areas (Li et al. 2011; Gao et al. 2007a, b), although a similar effect is not observed in pelagic water (Li et al. 2011). Global warming can significantly affect aquatic photosynthesis in different ways, by altering physical and chemical environmental conditions. First, warming of the upper ocean leads to stratification and to shoaling of the upper mixing layer. Phytoplankton cells in the upper mixing layer will be exposed to higher levels of solar UV radiation due to reduced mixing rate and depth. In this context, global warming and ozone depletion can act together to influence the primary producers. On the other hand, where higher contents of chemical constituents result in DOM-rich waters, ocean warming may stimulate photosynthesis by increasing the availability of limiting nutrients. The ongoing ocean acidification following enhanced dissolution of CO_2 may also interact with ocean warming and affect the primary production.

The photoinduced degradation of DOM and OM can produce H_2O_2, CO_2 and DIC (Molot et al. 2005; Johannessen et al. 2007; Mostofa and Sakugawa 2009; Mostofa et al. 2009b; Xie et al. 2004; Clark et al. 2004; Miller and Zepp 1995; Dillon and Molot 1997; Gennings et al. 2001; Johannessen and Miller 2001; Ma and Green 2004). Similarly, microbial degradation of DOM and OM yields for instance H_2O_2, CO_2, DIC, PO_4^{3-}, NH_4^+ and CH_4 (Mostofa and Sakugawa 2009; Ma and Green 2004; Fu et al. 2010; Palenik and Morel 1988; Lovley et al. 1996; Zhang et al. 2004, 2009; Kim et al. 2006; Li et al. 2008). The CO_2

and other compounds that are produced either photolytically (photoproducts) or microbially (microbial products), together with other environmental factors, may then influence photosynthesis (Mostofa et al. 2009a, b; Komissarov 1994, 1995, 2003):

Planktonic algae smaller than 5 μm are major fixers of inorganic carbon in the ocean (Li 1994) and dominate the phytoplankton biomass in post-bloom, stratified oceanic temperate waters (Tarran et al. 2001). Large and small phytoplankton cells have a critical and differential growth dependence on inorganic nutrients (Zubkov and Tarran 2008). UV-stimulated inorganic carbon acquisition is often observed in phytoplankton species (Beardall et al. 2009a, b; Wu and Gao 2009). Regeneration of autochthonous DOM and nutrients (NO_3^-, NO_2^-, PO_4^{3-} and NH_4^+) occurs during the photoinduced and microbial assimilation of algae or phytoplankton,and simultaneously also from the photoinduced degradation of DOM in natural waters (Mostofa et al. 2009a, b; Fu et al. 2005, 2010; Stedmon et al. 2007a, b; Ma and Green 2004; Kim et al. 2006; Li et al. 2008; Zhang et al. 2009; Carrillo et al. 2002; Mallet et al. 1998; Kopáček et al. 2004; Lehmann and Bernasconi 2004). Regeneration of nutrients significantly occurs in waters with high contents of DOM, which can control the uptake of nutrients during the photosynthetic process. Therefore, nutrients usually do not limit photosynthesis, particularly in waters with high contents of DOM. Primary production is enhanced significantly by DOM in the upper 30 m of the water column, where the production increase upon reduction of damaging UV radiation offsets the effects of attenuation of photosynthetically active radiation (PAR) (Arrigo and Brown 1996). At greater depths, where little UV radiation remains, primary production is often reduced due to removal of PAR by DOM (Arrigo and Brown 1996). When CDOM is distributed homogeneously within the euphotic zone, the depth-integrated daily primary productivity within the euphotic zone ($\int_z \mathrm{GPP}_{ez}$) is reduced under most bio-optical (i.e. solar zenith angle, Chl *a* and DOM absorption, ozone concentration) and photophysiological (i.e. sensitivity to UV radiation) conditions. In such cases, the predicted reduction in primary production at depth is greater than the enhancement of production at the surface (Arrigo and Brown 1996). The $\int_z \mathrm{GPP}_{ez}$ is decreased when DOM or phytoplankton is restricted to near-surface waters (−30 m) and it is enhanced when DOM or phytoplankton is restricted to a very shallow surface layer (−10 m) (Arrigo and Brown 1996). DOM effect on photosynthesis can also be justified from the observation of high primary productivity of phytoplankton biomass (Chl *a*) (Fig. 4a) and from the high photosynthetic carbon fixation rate (Fig. 4b, c) in coastal waters (usually with high contents of DOM) compared to pelagic ones (generally with low contents of DOM) (Li et al. 2011).

Another issue is the sustained photoinduced and/or microbial production of compounds such as H_2O_2, CO_2 and DIC in DOM-rich waters, which can enhance primary production (Mostofa and Sakugawa 2009; Mostofa et al. 2009b; Malkin et al. 2008; Ma and Green 2004; Meriläinen et al. 2001; Komatsu et al. 2007). Algae are significantly produced in some Chinese lakes during the summer stratification period, leading to high production of autochthonous DOM and nutrients (Mostofa et al. 2009b; Fu et al. 2010; Li et al. 2008). Such an effect is the consequence of high DOM contents that provide nutrients and simultaneously attenuate high solar radiation. Model results reveal that the progressive release of dissolved organic nitrogen (DON) in the ocean's upper layer during summer increases primary production by 30–300 %. This leads in turn to an enhancement of the dissolved organic carbon (DOC) production mainly from phytoplankton exudation in the upper layer and to solubilization of POM in the deeper layers (Druon et al. 2010).

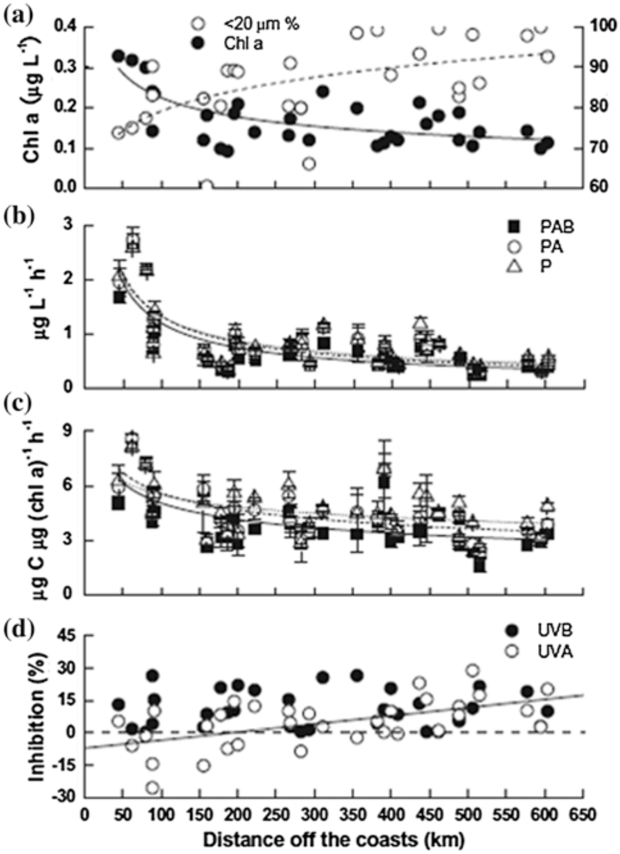


Fig. 4 Variations of biological characteristics in surface seawater from the coasts to pelagic waters. Phytoplankton biomass (Chl *a*, in μg L^{-1}) and piconanoplankton fractions (<20 μm, in %); the fitted lines are power functions ($Y = A\,x^{B}$, $R^2 = 0.47$ for Chl *a* and 0.32 for piconanofractions) (**a**); (**b**) and (**c**) Photosynthetic carbon fixation rates per volume of seawater (in μg C L^{-1} h^{-1}) (**b**) or based on Chl *a* [in μg C (μg Chl $a)^{-1}$ h^{-1}] (**c**) under PAR (P), PAR + UV-A (PA) or PAR + UV-A + B (PAB); the fitted lines are the power functions ($R^2 = 0.38$–0.63); Photosynthetic inhibition (in %) induced by UV-A or UV-B (**d**) where the solid line indicates the significant relationship between the UV-A-induced inhibition and the distance off the coast ($R^2 = 0.31$, $P < 0.01$, n = 32). Vertical bars present the standard deviations (n = 3). *Data source* Li et al. (2011)

UV-A does not enhance carbon fixation in pelagic (or oligotrophic) water because the picophytoplankton-dominated assemblages do not efficiently produce UV–absorbing compounds (Fig. 4) (Li et al. 2011; Garcia-Pichel 1994; Raven 1991). The UV-A related inhibition of carbon fixation increases from the coastal to pelagic waters, whereas UV-B impacts uniformly over time and space (Fig. 4d). Under reduced levels of solar radiation with heavy overcast, UV-A radiation enhances photosynthetic carbon fixation by up to 25 % in coastal waters where microplankton is abundant, but such a positive impact is not observed in offshore waters where piconanoplankton prevails (Li et al. 2011).

Water temperature, driven by solar radiation, is one of the crucial physical factors regulating photosynthesis in natural waters (Baulch et al. 2005; Mortain-Bertrand et al. 1988; Doyle et al. 2005; Yoshiyama and Sharp 2006). Primary production (approximately 67 % of variability) is mainly controlled by light availability and temperature. High nutrient concentrations do not stimulate primary production in estuary (Yoshiyama and Sharp 2006). Even the slight oceanic warming during the interglacials would result in increased affinity of active transport by algae and bacteria for nutrients (nitrate, phosphate and silicate) and would effectively increase the available pools of such nutrients in the oceans (Nedwell 1999). This increase in availability of nutrients with higher temperature would be predicted to enhance oceanic primary production and CO_2 drawdown during the interglacials (Nedwell 1999). Such a scenario is consistent with the data from the profiles of $\delta^{13}C$ isotopic ratios in benthic foraminiferan in Southern Ocean sediment cores. Such data suggest in fact increased interglacial oceanic production (Broecker and Peng 1993; Neori and Holm-Hansen 1982). It is also shown that the highest NH_4 concentrations are detected in the colder months when temperature and daily irradiance are lower, but primary production does not increase linearly with ammonium (Yoshiyama and Sharp 2006). Global warming may lengthen the summer season and enhance the water column transparency with modification of the depth of the mixing layer or euphotic zone. Such processes would influence the doses of UV radiation and PAR received by the phytoplankton cells (Malkin et al. 2008; Scully and Lean 1994; Morris et al. 1995; Morris and Hargreaves 1997). The consequence could be a photoinhibition of the cells within the upper layer in sunny days. Enhanced photosynthetic rates of polar phytoplankton are observed in response to increasing temperatures (Broecker and Peng 1993; Neori and Holm-Hansen 1982; Reay et al. 2001; Jacques 1983). This effect ultimately causes an increase in photosynthesis in natural waters, in particular in the deeper layers, because of an enhancement in its duration.

Global warming can also induce an increase in DOM contents in natural waters because of enhanced DOM leaching from terrestrial soils connected to high soil respiration following elevated atmospheric CO_2 concentrations (Porcal et al. 2009). Global warming can enhance the photosynthesis of terrestrial plants becuase of higher atmospheric CO_2 levels, which results in high primary production. The parallel increase of atmospheric temperature would also increase the soil respiration (Porcal et al. 2009; Freeman et al. 2001, 2004; Tranvik and Jasson 2002;

Evans et al. 2005, 2006; Roulet and Moore 2006; de Wit et al. 2007; Monteith et al. 2007; Dorodnikov et al. 2011). The decomposition of soil OM by microbial biomass is significantly increased under elevated atmospheric CO_2 (Dorodnikov et al. 2011; Heath et al. 2005; Lagomarsino et al. 2009; Blagodatskaya et al. 2010, 2011). High turnover rates of soil OM are apparently driven by the increasing activity of soil microorganisms under elevated CO_2 conditions (Blagodatskaya et al. 2010, 2011; Dorodnikov et al. 2009). It is also shown that the increasing activity of soil microorganisms under elevated CO_2 could accelerate the decomposition of older and fresh plant residues (Dorodnikov et al. 2009, 2011; Blagodatskaya et al. 2010; Marhan et al. 2010). In addition, the labile organic carbon released by roots stimulates microbial activity, leading to enhanced degradation of soil OM. This process is known as the ‘priming mechanism’ (Kuzyakov 2002). Elevated CO_2 can enhance soil organic matter mineralization by 83–218 % in a simulated wetland (Wolf et al. 2007). Therefore, elevated atmospheric CO_2 concentrations could enhance both primary production and soil respiration, inducing increased export of DOC to nearby natural waters (Porcal et al. 2009).

4.5 Changes in the Primary Production and Disorders in Chlorophyll a *Maxima*

Global warming may affect the seasonal patterns of primary production, the chlorophyll concentrations in the surface chlorophyll *a* maxima (SCM) and in the deep chlorophyll *a* maxima (DCM) in natural waters (Letelier et al. 2004; Huisman et al. 2006; Mostofa et al. 2009b; Baulch et al. 2005; Castle and Rodgers 2009; Davis et al. 2009; Hobson and McQuoid 2001). It is estimated that, depending on location, ambient UV radiation can reduce carbon fixation rates up to 65 % in surface waters of the Antarctic region, down to undetectable levels at 36 m (Boucher and Prézelin 1996). A reduction of stratospheric O_3 concentrations by 50 % would further inhibit the near-surface primary production by 8 % and the integrated primary production by 5 % (Boucher and Prézelin 1996). This effect causes the occurrence of subsurface maxima of primary production in the presence of UVR (Boucher and Prézelin 1996). About 67 % of the variability of the observed primary production indicates that estuarine production is mainly controlled by light availability and temperature. In contrast, high nutrient concentrations do not stimulate primary production (Yoshiyama and Sharp 2006).

Global warming will increase the stability of the vertical stratification in large parts of the lakes and oceans, reducing vertical mixing and suppressing the upward flux of nutrients. The effect would be a decrease in primary production (O’Reilly et al. 2003; Huisman et al. 2006). Reduced vertical mixing can generate oscillations and chaos in phytoplankton biomass and species composition of DCM, which is generated by the difference in timescale between the sinking flux of phytoplankton and the upward flux of nutrients (Huisman et al. 2006; Barbiero and Tuchman 2004). The increased stability of the water column due to global warming can thus destabilize phytoplankton dynamics in both DCM and SCM. The actual effect can be different in different types of water. Waters with low contents of DOM (apparently <100 mM C) can yield low contents of photo- and microbial products (H_2O_2, CO_2, DIC) in the euphotic zone, with limited enhancement of productivity. This effect is often found in the oligotrophic regions of the ocean where the nutrient-poor upper layer is made even poorer as a result of enhanced stratification. The phenomenon has a negative impact on net primary production and can produce oceanic 'oligotrophication' as a direct effect of global warming (Sarmento et al. 2010; Falkowski and Oliver 2007; Falkowski and Wilson 1992; Karl et al. 2001; Polovina et al. 2008; Behrenfeld et al. 2006).

A regional decrease in wind velocity in Lake Tanganyika, East Africa has contributed to reduced mixing, decreasing the deep-water nutrient upwelling and entrainment into surface waters (O'Reilly et al. 2003).

Increased stability of the water column may enhance the photoinduced degradation of DOM by combination of high temperature and longer summer season. In waters with high contents of DOM this would lead to the production of high contents of photo- and microbial products (such as H_2O_2, CO_2 and DIC). This process enhances photosynthesis and can result into in high primary production. Phytoplankton or algae productivity in DOM-rich waters would also enhance the production of autochthonous DOM and nutrients (Mostofa et al. 2009b; Stedmon et al. 2007a, b; Malkin et al. 2008; Fu et al. 2010; Li et al. 2008; Zhang et al. 2009; Carrillo et al. 2002; Kopáček et al. 2000, 2004). High production of further DOM and nutrients would severely worsten the quality of waters with high contents of DOM, particularly in lakes, reservoirs, estuaries, coastal waters and in the Arctic and Antarctic regions. Such effects of climate warming may simultaneously promote harmful algal blooms or toxic phytoplankton populations (Davis et al. 2009; Mudie et al. 2002; Richardson and Jorgensen 1996; Hallegraeff 1993; Harvell et al. 1999; Braun and Pfeiffer 2002). The occurrence of cyanobacterial blooms in freshwater has increased over the last few decades all over the world (Xu et al. 2000; Chen et al. 2003; McCarthy et al. 2007).

An increase in dissolved primary production is one of the consequences of the temperature rise in the Southern Ocean (Morán et al. 2006). Similar processes in subarctic lakes are likely to result in higher DOC concentration, bacterial production and respiration, and into emission of CO_2 to the atmosphere (Jansson et al. 2008).

The penetration to significant depths of solar UV radiation can affect arthropods, cyanobacteria, phytoplankton, macroalgae and aquatic plants in both freshwater and marine environments, including Antarctic and Arctic waters (Ballaré et al. 2011; Huisman et al. 2006; Häder et al. 2003, 2007, 2011; Karl et al. 2001; Sinha et al. 2001; Day and Neale 2002; Frenot et al. 2005; Rastogi et al. 2010). Changes in the timing of primary producers, possibly forced by UV-B radiation and temperature increase, would change connectivity in the food web among phytoplankton, zooplankton, crustaceans, amphibians, fish, corals and birds (Kitaysky and Golubova 2000; Morrison et al. 2002; Johannessen and Macdonald 2009; Häder et al. 2007, 2011; Pomeroy and Wiebe 2001).

The primary producers (e.g. phytoplankton cells) tend to be smaller in a warmer ocean (Falkowski and Oliver 2007; Daufresne et al. 2009; Morán et al. 2010). It has also been shown that UV-B influences the CO_2-concentrating mechanism of *M. aeruginosa*, and this cyanobacterium has many adaptive strategies to cope with prolonged UV-B exposure (Jiang and Qiu 2005; Song and Qiu 2007). Enhanced solar UV-A (315–400 nm) and/or UV-B radiation (280–315 nm) can reduce growth and photosynthetic rates, inhibit pigment production, increase permeability of cell membranes, damage proteins or DNA molecules, and even lead to cell death (Jiang and Qiu 2005, 2011; Behrenfeld et al. 1993; Sass et al. 1997; Helbling et al. 2001; Buma et al. 2003; Sobrino et al. 2004; Litchman and Neale 2005; Wu et al. 2005; Agustí and Llabreés 2007; Rath and Adhikary 2007; Pattanaik et al. 2008; Gao et al. 2008). At normal ozone concentrations (i.e. 344 Dobson Units), UV radiation can reduce primary productivity in surface waters by as much as 50 % (Cullen et al. 1992; Holm-Hansen et al. 1993b; Cullen and Neale 1994). A normal level of UV radiation also reduces phytoplankton production by 57 % at a depth of 1 m, while such inhibition decreases to <5 % at 30 m, at 50ºS in mid December (Arrigo 1994). Such effects on aquatic organisms might be caused directly by UV radiation and indirectly through high production of $HO^{\bullet}$ in epilimnetic (upper layer) waters. Both effects are able to alter the structural configuration of organisms with release of many organic substances in epilimnetic (surface layer) waters (Mostofa et al. 2009a, b; Sinha et al. 2001; Rastogi et al. 2010; Gauslaa and McEvoy 2005; Lesser 2008; Hylander et al. 2009; Ingalls et al. 2010).

To conclude, global warming may greatly impact primary production, species composition, carbon export, and finally biological activities in the aquatic environment (Huisman et al. 2006; Häder 2011; Häder et al. 2003, 2007; Sinha et al. 2001; Rastogi et al. 2010; Petchey et al. 1999).

4.6 Changes in DOM Dynamics and the Global Carbon Cycle

The increase of DOC concentration in many catchments in Europe and North America might be the concequence of a climate effect (Zepp et al. 2011; Burns et al. 2006; Vuorenmaa et al. 2006; Sobek et al. 2007; Zhang et al. 2010; Freeman et al. 2001, 2004; Evans et al. 2005; Skjelkvåle et al. 2001; Löfgren et al. 2003; Hongve et al. 2004; Worrall et al. 2005; Larsen et al. 2011). An increase of DOC in natural waters because of global warming could be linked to the production of autochthonous DOM by phytoplankton or algae under both photoinduced and microbial-assimilation (Johannessen et al. 2007; Mostofa et al. 2009a, b; Fu et al. 2005, 2010; Stedmon et al. 2007a; Zhang et al. 2009; Biddanda and Benner 1997; Carrillo et al. 2002; Mallet et al. 1998; Lehmann and Bernasconi 2004). Indeed, increasing temperature can increase the release of organic substrates by phytoplankton (Morán et al. 2006; Watanabe 1980; Verity 1981; Zlotnik and Dubinsky 1989). Such phenomena can in turn enhance photosynthesis and primary production, as already explained, particularly in DOM-rich waters.

On the other hand, global warming can affect waters with low contents of DOM in the opposite direction, inhibiting the production of various compounds that ultimately limit photosynthesis and primary production. This effect can proceed either by gradually decreasing the total contents of DOM and nutrients or by reducing the nutrients at equal DOM. The latter scenario can occur because in waters with low contents of DOM, as can be found for instance in Lake Biwa and Lake Baikal, allochthonous DOM usually dominates than autochthonous DOM (Yoshioka et al. 2002; Mostofa et al. 2005). The removal of total organic carbon (total internal and external inputs) is accounted for by respiration (50 %), sedimentation (40 %) and photo-oxidation (10 %) in acidic lakes (Kopáček et al. 2004).

Production of algae or phytoplankton and the related photoinduced and microbial release of new DOM are greatly influenced by several factors, such as high precipitation (Zhang et al. 2010; Freeman et al. 2001; Tranvik and Jasson 2002; Hejzlar et al. 2003), land use changes that induce high transport of DOC from catchments to adjacent surface waters (Worrall et al. 2004; Raymond and Oh 2007), nitrogen deposition (Pregitzer et al. 2004; Findlay 2005), sulfate deposition (Zhang et al. 2010; Evans et al. 2006; Monteith et al. 2007), drought and alteration of hydrologic pathways (Zhang et al. 2010; Hongve et al. 2004; Knorr et al. 2005), and change in total solar UV radiation or increase in temperature due to global warming (Sobek et al. 2007; Zhang et al. 2010; Freeman et al. 2001; Sinha et al. 2001; Rastogi et al. 2010). Higher temperatures in the tropical zone may accelerate bacterial metabolism, causing a larger fraction of incoming organic carbon to be respired (Tranvik et al. 2009). In temperate zones, the additive effect of decreased water availability and increased primary production may enhance organic carbon burial through increased autochthonous production and preservation (Cotner and Biddanda 2002; Downing et al. 2008). A recent study of DOC concentrations in over 7,500 lakes in six continents suggests that DOC export is potentially enhanced by global warming in aquatic ecosystems (Sobek et al. 2007). It has also been shown that total solar radiation and precipitation can account for 49–84 % of the variation in the long-term DOC patterns in various catchments (Zhang et al. 2010). DOC concentrations in Swedish lakes and streams have substantially increased during 1970–1980, despite a reduction in temperature, most likely because of higher precipitation (Tranvik and Jasson 2002).

The uptake of inorganic nitrogen by bacteria during a phytoplankton bloom occurs particularly in lake or coastal waters where the inputs of terrestrial humic substances are much higher (Kirchman et al. 1991; Amon and Benner 1994). Photolytically produced ammonium can be assimilated by bacterial populations, which can enhance the production of autotrophic and heterotrophic biomass in planktonic environments.

Carbon storage in high-latitude peatlands is estimated to represent one-third or more of the global soil carbon pool (Post et al. 1982; Zimov et al. 2006). Warming-induced decomposition of soil organic matter, particularly in arctic and subarctic soils (Anderson 1991), can result in greater transport of allochthonous DOC to adjacent natural waters. Water bodies that usually received low DOC inputs such as alpine lakes or those resulting from glacial retreat may be strongly affected by the altered DOC quality, which causes for instance the replacement of herbs by less productive shrubs (Shaver et al. 2000).

Beneath the sea ice in the Central Basin, relatively high values of $p\mathrm{CO}_2$ have been detected, ranging between 425 and 475 μatm values. Such values are larger than the mean atmospheric one in the Arctic in summertime, suggesting that CO_2 might derive from high rates of bacterial respiration (Semiletov et al. 2007). Ambient partial pressure values of CO_2 ($pCO_2 = 21\text{–}73.5$ Pa) are produced during the coral reef metabolism in Eastern Pacific reef sites. Such values are highly variable depending on depth, time, space and upwelling-nonupwelling period (Manzello 2010).

Photoinduced and microbial degradation of DOM and OM is a source of atmospheric greenhouse gases such as CO_2 and CH_4, thereby contributing to global carbon cycle and further global warming (Porcal et al. 2009; Knorr et al. 2005; Davidson and Janssens 2006). Elevated CO_2 enhances DOC supply in peat soils, an effect that is attributed to elevated net primary productivity and increased root exudation of DOC. Enhanced DOC in soil will ultimately leach into aquatic ecosystems (Freeman et al. 2004; Barbiero and Tuchman 2004; Kang et al. 2001; Pastor et al. 2003; Lavoie et al. 2005; Fenner et al. 2007a, b). Global warming could also increase soil respiration (Freeman et al. 2001, 2004; Tranvik and Jasson 2002; Evans et al. 2005, 2006; Roulet and Moore 2006; de Wit et al. 2007; Monteith et al. 2007; Dorodnikov et al. 2011).

Freshwater ecosystems that are presently located across vegetation gradients will experience significant shifts in underwater spectral irradiance. The main reasons are the effects of climate change on catchment vegetation and the export of colored DOM (Pienitz and Vincent 2000). Overall, elevated atmospheric CO_2 concentrations would increase primary production, with a consequent increase of the decomposition of soil OM and an increased export of DOC to nearby natural waters (Porcal et al. 2009). These processes can also contribute to enhance the DOM contents in natural waters.

4.7 Changes in Nutrients Cycle

The mass balance of nutrients (NO_2^-, NO_3^-, NH_4^+ and total P) is linked with the major external inputs (terrestrial and atmospheric deposition), internal sources and transformations (primary and bacterial production, secondary production, photo- and/or microbial-assimilation of algae or phytoplankton and plant debris), photoinduced transformation of both external and internal sources of nutrients, nitrification, sedimentation and outputs in natural waters (Mostofa et al. 2009b; Fu et al. 2005; Minero et al. 2007; Stedmon et al. 2007a, b; Sterner et al. 2008; Ma and Green 2004; Zhang et al. 2004; Kim et al. 2006; Li et al. 2008; Carrillo et al. 2002; Mallet et al. 1998; Kopáček et al. 1995, 2000, 2004; Lehmann and Bernasconi 2004; Schindler 1988, 1994; Carlsson et al. 1993; Urabe 1993; Bushaw et al. 1996; Goldman et al. 1996; Ramm and Scheps 1997; Mack and Bolton 1999; Sterner and Elser 2002; Demott 2003; Xie et al. 2003; Kopáček et al. 2003; Ahlgren et al. 2005). Coastal waters are generally nutrient-rich whereas open oceans are often oligotrophic, thus they are usually less productive due to nutrient limitation (Kolber et al. 1990; Shen 2001; Falkowski et al. 2004; Ho et al. 2008). Nutrient enrichment is a common feature in lakes, estuaries and coastal oceans worldwide, which can be the primary cause of eutrophication from excess algal growth (Yoshiyama and Sharp 2006; Smith 2003). Large amounts of nutrients (NO_3^-, NH_4^+ and total P or PO_4^{3-}) are produced from photoinduced and microbial-assimilations of algae or phytoplankton biomass, as well as by photoinduced degradation of DOM in natural waters (Stedmon et al. 2007a, b; Fu et al. 2010; Kim et al. 2006; Li et al. 2008; Kopáček et al. 2004; Kopáček et al. 2003). Formation of N-containing (NH_4^+, NO_3^-, and NO_2^-) and P-containing inorganic compounds (PO_4^{3-}) may take place upon degradation of dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) in the epilimnion of natural waters (Mostofa et al. 2011; Zhang et al. 2004; Kim et al. 2006; Li et al. 2008; Bronk 2002; Vähätalo and Järvinen 2007). DIC is also produced both photolytically and microbially from DOM in natural waters (Granéli et al. 1996; Ma and Green 2004; Miller and Moran 1997; Bertilsson and Tranvik 2000). Seasonal and long-term variations of N-containing compounds in natural waters are influenced by biological processes, in which uptake by algae or phytoplankton and denitrification in bottom water play a major role (Seitzinger et al. 2006). It is therefore suggested that algae or phytoplankton might be the key controlling factors that determine the total content of nutrients in natural waters.

Global warming could cause a loop by significantly increasing the photoinduced degradation of DOM with high production of photoproducts (e.g. CO_2, DIC, H_2O_2), which can enhance photosynthesis and primary production. The effect is a higher production of nutrients, particularly in waters with high DOM contents. Therefore, global warming could lead to a considerable eutrophication of already DOM-rich waters.

The nutrients from external inputs (terrestrial and atmospheric deposition) and sedimentation sources are expected to play a less important role toward primary production. Indeed, high contents of nutrients are observed in waters with high contents of DOM or chlorophyll *a* (Stedmon et al. 2007a, b; Fu et al. 2010; Li et al. 2008; Carrillo et al. 2002; Kopáček et al. 2000, 2004). At the same time, N-compounds are strongly dependent on climatic factors in natural waters (Mitchell et al. 1996; Murdoch et al. 1998; Weyhenmeyer 2008; Hessen et al. 2009). An increase in temperature and changes in the precipitation regime can affect biological processes in soil and water, which are involved into the retention and release of N (Windolf et al. 1996; Khalili and Weyhenmeyer 2009). On the other hand, waters with low contents of either DOM or chlorophyll *a* often show low contents of nutrients that typically remain the same for long periods (Kim et al. 2006; Goldman et al. 1996; Fott et al. 1994; Vyhnálek et al. 1994; Sugiyama et al. 2005). These processes are affected by water temperature, thus climate parameters may exert a major control on nutrient variability in natural waters. Global warming could thus modify the seasonal patterns of nutrient concentrations in the water column of lakes and oceans (Letelier et al. 2004; Huisman et al. 2006). High concentrations of nutrients due to global warming could thus severely deteriorate the quality of DOM-rich waters.

5 Conceptual Model for the Impacts of Global Warming on Key Biogeochemical Processes

From the previous discussion of the ‘Impacts of global warming on natural waters’ section, it is possible to summarize the key biogeochemical steps that take place in natural waters. First, photoinduced transformation induced by natural sunlight is the primary step for the photo-induced generation of oxidizing species (e.g. H_2O_2 and $HO^{\bullet}$) from DOM and chemical species (such as NO_2^- and NO_3^-). Such processes can drive the photoinduced degradation of DOM in surface waters (Fig. 5), yielding a variety of photoproducts among which H_2O_2, CO_2 and DIC. Second, photosynthesis is enhanced by the occurrence of the cited photoproducts in the euphotic zone, with a subsequent increase of the primary production (algae or phytoplankton). Third, primary productivity further induces photoinduced and microbial assimilations that release autochthonous DOM and nutrients. Fourth, autochthonous DOM and nutrients undergo photoinduced and microbial degradation that further yields H_2O_2, CO_2 and DIC. Global warming can thus favor the photosynthesis and, as a consequence, the primary production.

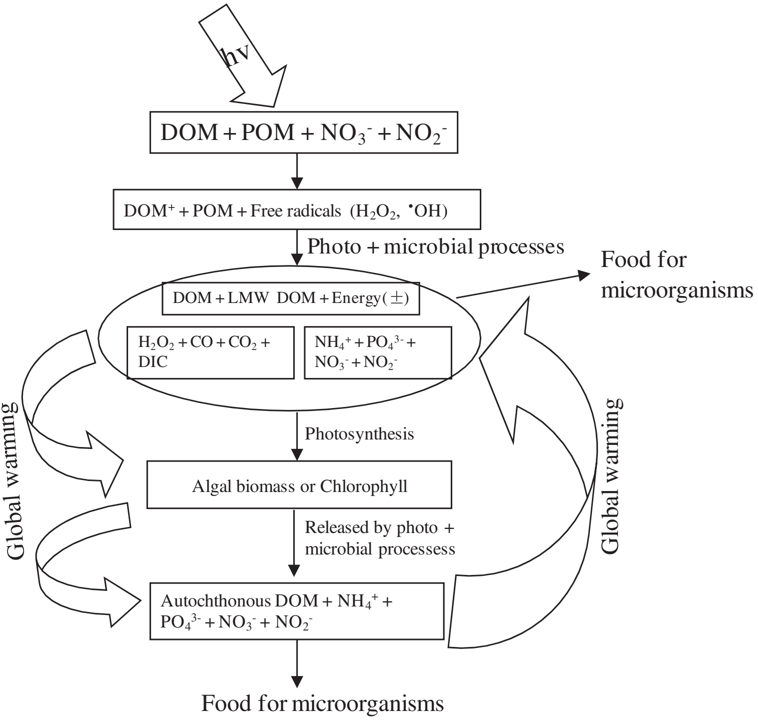


Fig. 5 Conceptual model on photochemical degradation of DOM and its possible effects on key biogeochemical processes in natural waters in response to global warming. *Data source* with few modifications Mostofa et al. (2009b)

The described processes (Fig. 5) are more important in waters having high contents of DOM, naturally or because of pollution, and can lead to further eutrophication of DOM-rich waters. The process would be enhanced by the extension of the summer season and of the euphotic zone that is expected to take place because of global warming. Total contents of DOM and global warming together thus severely affects on foodwebs, primary productivity, and nutrients cycles in freshwater environments which ultimately impact on drinking water quality, sustainable uses of agriculture and industrial purposes as well as the whole water ecosystem (Mostofa et al. 2009b; Li et al. 2008; Larsen et al. 2011; Hessen et al. 1990; Ask et al. 2009; Karlsson et al. 2009). The importance of the described processes would be much lower in DOC-poor (oligotrophic) systems. In such cases other phenomena could play a more important role, and the enhanced photoinduced DOM degradation could even lead to a further oligotrophication of DOC-poor systems.

The photoinduced degradation of DOM generally takes place through redox reactions that can lead to supply (+) or consumption (−) of energy in natural waters. Energy changes (±) also occur during photosynthesis (Komissarov 1994, 1995, 2003). DOM with its content of organic C and N is a thermodynamic anomaly that provides a major source of energy to drive aquatic and terrestrial ecosystems (Wetzel 1984, 1992; Salonen and Vähätalo 1994; Tranvik 1992; Hedges et al. 2000). Therefore, any changes in energy during the photoinduced degradation of DOM are thermodynamically vital for all the living organisms and for the aquatic environments.

The photoinduced degradation of DOM is interlinked free radical production, microbial processes, photosynthesis, autochthonous DOM, nutrients, end photoproducts and their utilization as food for microorganisms in natural waters. A conceptual schematic diagram for the global warming effects on photoinduced and microbial processes of DOM and POM, photoproducts and their importance in the aquatic environment is depicted below (Fig. 5):

Finally, it can be concluded that any changes in nature are absolutely interlinked with other changes in the natural ecosystem.

5.1 Remedial Measures for Controlling Algal Blooms due to Global Warming

The possible remedial measures for controlling the lake algal blooms that are severely affecting the water quality because of global warming are listed below: (i) The total DOM contents in lake waters should be reduced by applying coagulation processes that can reduce the regeneration of photoproducts, microbial products and nutrients. Such measures would thus reduce photosynthesis and, as a consequence, the primary production (algae or phytoplankton) in natural waters. During the algal blooms, algae or phytoplankton should be removed using fine, small-mesh nets. Such a procedure could reduce the further photoinduced and microbial release of DOM and nutrients from primary production. The consequence would be a significant reduction of further photosynthesis and, thus, of primary production. (ii) The sediments in the lake bottom should be removed, which will reduce to pore water's DOM and nutrients and their transport to surface waters, a phenomenon that generally occurs during the overturn period or because of any other physical processes. (iii) Erosion should be reduced in the surrounding soil environments, because erosion can enhance the allochthonous DOM, POM and nutrient contents of natural waters. Erosion can be reduced by proper plantation in the surrounding soils of the watershed.

6 Challenges for Future Research

Global warming is expected to enhance primary production in Chinese lakes and reservoirs, which could severely deteriorate water quality and considerably impact the sustainable use of freshwater resources. Concurrently, DOM contents have been gradually increasing in some European lakes in the last few decades, possibly because of the effect of global warming. Global warming could lead to considerable eutrophication of DOM-rich waters, by gradually increasing the occurrence of autochthonous DOM and nutrients and severely deteriorating the water quality. On the other hand it can affect DOM-poor waters, either inducing a gradual decrease of the total contents of DOM and nutrients or maintaining the same range of DOM levels but causing the nutrients to decline.

The global warming has been found to increase the average Arctic temperatures at almost twice the global average rate in the past 100 years. Therefore, warming is expected to significantly impact the biogeochemical processes of Arctic and Antarctic regions. Therefore, a number of important researches can be distinguished as: (i) Monitoring the contents of DOM and nutrients in natural waters affected by global warming. (ii) Extensively studying the photoinduced and microbial release of autochthonous DOM and nutrients from DOM and algae or phytoplankton in natural waters. (iii) Investigating the photoinduced and microbial release of CO_2, DIC and H_2O_2 from autochthonous DOM, algae or phytoplankton in natural waters. (iv) Studying the photoinduced and microbial release of autochthonous DOM from algae or phytoplankton in Arctic and Antarctic waters. (v) Development of remedial measures for high primary production caused by global warming in waters with high contents of DOM. (vi) Finally, development of remedial measures for low primary productivity caused by global warming in waters with low contents of DOM.

7 Nomenclature

CO_2	Carbon dioxide
DIC	Dissolved inorganic carbon (DIC: dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-})
DOM	Dissolved organic matter
GHGs	Green house gases

GWPs	Global warming potentials
H_2O_2	Hydrogen peroxide
IPCC	Intergovernmental Panel on Climate Change
Kyr	Kilo year (1000 year)
CH_4	Methane
OM	Organic matter
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
POM	Particulate organic matter
PO_4^{3-}	Phosphate
UNFCCC	United Nations Framework Convention on Climate Change
UV	Ultraviolet
Yrs	Years

Problems

(1) What is global warming? List the atmospheric greenhouse gases and other constituents which contribute to global warming.
(2) Explain how atmospheric greenhouse gases increase global warming.
(3) Explain how the atmospheric sulfate aerosols could reduce the global warming.
(4) Explain how the stratospheric ozone depletion affects global warming and natural water chemistry.
(5) Explain the contributions of atmospheric greenhouse gases to global warming.
(6) What is radiative forcing by greenhouse gases? Explain how global warming potentials become indicators of global warming.
(7) How are the environmental processes of greenhouse gases emission affected by global warming? Explain how global warming enhances the soil respiration that releases atmospheric greenhouse gases.
(8) Explain the various processes of CO_2 emission during agricultural activities.
(9) How does deforestation affect global warming?
(10) Explain where and why the emissions of CO_2 occur by photoinduced degradation of DOM in natural waters.
(11) What are the possible impacts of global warming on physical, chemical and biological processes in natural waters?
(12) Explain how does global warming affect photoinduced and microbial activities in natural waters.
(13) Explain how does global warming affect photosynthesis and primary productivity in natural waters.
(14) Explain why and how does global warming impact on waters with high contents of DOM.

(15) Explain the global warming impact on the DOM dynamics in natural waters.
(16) What are the sources of nutrients in natural waters and how does the global warming impact the aquatic nutrient dynamics?
(17) Explain the conceptual model for the impact of global warming on key biogeochemical processes in natural waters.

Acknowledgments We thank Dr. Benjamin Chetelat of Institute of Geochemistry, Chinese Academy of Sciences for his helpful assiatnce during the manuscript preparation. This work was financially supported by the Institute of Geochemistry, the Chinese Academy of Sciences, China. This work was partly supported by Xiamen University, China; University Turin, Itali; and Northwest Missouri State University, USA. This chapter acknowledges the reprinted from Soil Biology & Biochemistry 41(4), Feng X, Simpson MJ, Temperature and substrate controls on microbial phospholipid fatty acid composition during incubation of grassland soils contrasting in organic matter quality, 804–812, Copyright (2009), with permission from Elsevier; Li G, Gao K, Gao G, Differential Impacts of Solar UV Radiation on Photosynthetic Carbon Fixation from the Coastal to Offshore Surface Waters in the South China Sea, Photochemistry and Photobiology, Copyright (2011) by Wiley-Blackwell, Inc; Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Figs. 1.1 and 2.3. IPCC, Geneva, Switzerland; and Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, Table 3. Cambridge University Press.

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