

# Individual and interactive effects of ocean acidification, global warming, and UV radiation on phytoplankton

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**Abstract** Rising carbon dioxide (CO<sub>2</sub>) concentrations in the atmosphere result in increasing global temperatures and ocean warming (OW). Concomitantly, dissolution of anthropogenic CO<sub>2</sub> declines seawater pH, resulting in ocean acidification (OA) and altering marine chemical environments. The marine biological carbon pump driven by marine photosynthesis plays an important role for oceanic carbon sinks. Therefore, how ocean climate changes affect the amount of carbon fixation by primary producers is closely related to future ocean carbon uptake. OA may upregulate metabolic pathways in phytoplankton, such as upregulating β-oxidation and the tri-carboxylic acid cycle, resulting in increased accumulation of toxic phenolic compounds. Ocean warming decreases global phytoplankton productivity; however, regionally, it may stimulate primary productivity and change phytoplankton community composition, due to different physical and chemical environmental requirements of species. It is still controversial how OA and OW interactively affect marine carbon fixation by photosynthetic organisms. OA impairs the process of calcification in calcifying phytoplankton and aggravate ultraviolet (UV)-induced harms to the cells. Increasing temperatures enhance the activity of cellular repair mechanisms, which mitigates UV-induced damage. The effects of OA, warming, enhanced exposure to UV-B as well as the interactions of these

environmental stress factors on phytoplankton productivity and community composition, are discussed in this review.

**Keywords** Ocean acidification · Ocean warming · Photosynthesis · Phytoplankton · Primary producers · UV radiation

## Introduction

Anthropogenically induced global environmental changes and natural variability are altering terrestrial and aquatic environments and ecosystems, affecting the sustainable development of resources for a rapidly increasing human population (Lammers et al. 2013). Increasing release of CO<sub>2</sub> from fossil fuel burning, tropical deforestation, and other sources results in ocean acidification (Zeebe 2012) and global warming (IPCC 2014) which leads to increases in sea level (Nick et al. 2013) and alteration in water mixing dynamics (Ehlert et al. 2017). The oceans are a major sink for atmospheric CO<sub>2</sub> and therefore a major player in the global change partially mitigating temperature increases (Landschützer et al. 2014). The main mechanism for removing CO<sub>2</sub> in the water is the biological carbon pump (Honjo et al. 2014). Prokaryotic and eukaryotic primary producers in the oceans absorb CO<sub>2</sub> and fix it via photosynthesis to generate organic matter. Marine productivity, mainly by phytoplankton, accounts for about 50% of the global primary production (Field et al. 1998). These organisms form the basis of the oceanic food webs, supporting, directly and indirectly, most marine consumers including microbes and metazoans. Organic material in the form of dead organisms and fecal pellets sediment as “oceanic snow” to the deep sea bottom and add to the largest carbon reservoir on the planet (IPCC 2014).

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Global warming caused by increasing atmospheric CO<sub>2</sub> and methane concentrations results in increasing surface seawater temperatures enforcing stratification and shoaling of the upper mixed layer (UML) above the thermocline (Boyce et al. 2010; Wang et al. 2015). This exposes the organisms dwelling in this layer to excessive solar visible (PAR) and UV radiation (UVR) (Gao et al. 2012a, 2012b). In addition, the augmented stratification hinders the transport of dissolved inorganic macronutrients from deeper waters into the UML (Behrenfeld et al. 2006). On the other hand, rising temperatures increase metabolic functions in phytoplankton and may mitigate UV-B-inflicted damage by increasing the repair mechanisms in the cells (Häder et al. 2015).

While stratospheric ozone depletion has been stalled and there are signs of a recovery in the Antarctic Ozone Hole due to the effects of the Montreal Protocol, increased levels of UV-B (280–315 nm) still prevail due to the long lifetimes of CFCs (chlorinated fluorocarbons) in the stratosphere (on the order of many decades) (McKenzie et al. 2011; Newman and McKenzie 2011; Solomon et al. 2016). In addition, HCFCs (chlorodifluoromethane) have a small but noticeable ozone depletion potential, and their concentrations are increasing because they are used as substitutes for CFCs (Wallington et al. 1994). It is assumed that UVR will decrease at mid- and high latitudes relative to the 1960s, but the trend in the tropics may depend on the emission of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O (Bais et al. 2015). However, simulations based on a chemistry-climate model indicated that the total ozone might be lower in the tropics compared to the 1960s (United Nations Environment Programme Environmental Effects Assessment Panel 2017). For these reasons, the eco-physiological effects of the enhanced UV-B radiation continue to rouse increasing attention (Häder and Gao 2015).

Ocean acidification, warming, and enhanced exposure to excessive PAR and UVR have positive and negative effects on phytoplankton productivity and community structure (van Wells et al. 2015; Domingues et al. 2017). This review describes the individual and interactive effects of these ecological stress factors on ecologically and economically important marine primary producers.

### Ocean acidification and its effect on phytoplankton

The uptake of CO<sub>2</sub> from the atmosphere depends on temperature, salinity, mixing intensity, and chemistry of surface seawater that interacts with biological activities. The decline of surface ocean pH due to dissolution of anthropogenic CO<sub>2</sub> results in ocean acidification (OA) (Caldeira and Wickett 2003). In the upper mixing layer (UML), the average lifetime of dissolved CO<sub>2</sub> is about 6 years while the exchange between epipelagic and mesopelagic seawater (1000–4000 m depth) requires hundreds of years (Raven et al. 2005). Sabine et al.

(2004) calculated that the oceans have absorbed more than 30% of the anthropogenically released CO<sub>2</sub>, thereby partially mitigating global warming. Combustion of fossil fuel and tropical deforestation results in an increase of atmospheric CO<sub>2</sub>. This is further augmented by a feedback mechanism resulting from a release of CO<sub>2</sub> and methane from thawing permafrost areas in the Arctic due to rising global temperatures (Schädel et al. 2016). Since more than half of the CO<sub>2</sub> absorbed by the oceans remains in the surface layer (0–400 m), OA accelerates with declining capability to take up the CO<sub>2</sub> (Sabine et al. 2004). With increasing atmospheric CO<sub>2</sub> concentrations up to 1000 ppmv under the business-as-usual scenario (RCP8.5), the pH of surface oceans is predicted to drop by 0.4 units, indicating an increase of H<sup>+</sup> ions by about 150% (Zeebe and Wolf-Gladrow 2001; Caldeira and Wickett 2003; Gattuso et al. 2015).

As CO<sub>2</sub> reacts with water, it forms carbonic acid which dissociates into H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>:



The latter product further dissociates into H<sup>+</sup> and CO<sub>3</sub><sup>2-</sup>:



The equilibrium constants of these three reactions depend on salinity and temperature in the surface waters. As the concentration of H<sup>+</sup> increases in Eq. 2, reaction 3 is shifted to the left, resulting in a decrease of the CO<sub>3</sub><sup>2-</sup> concentration.

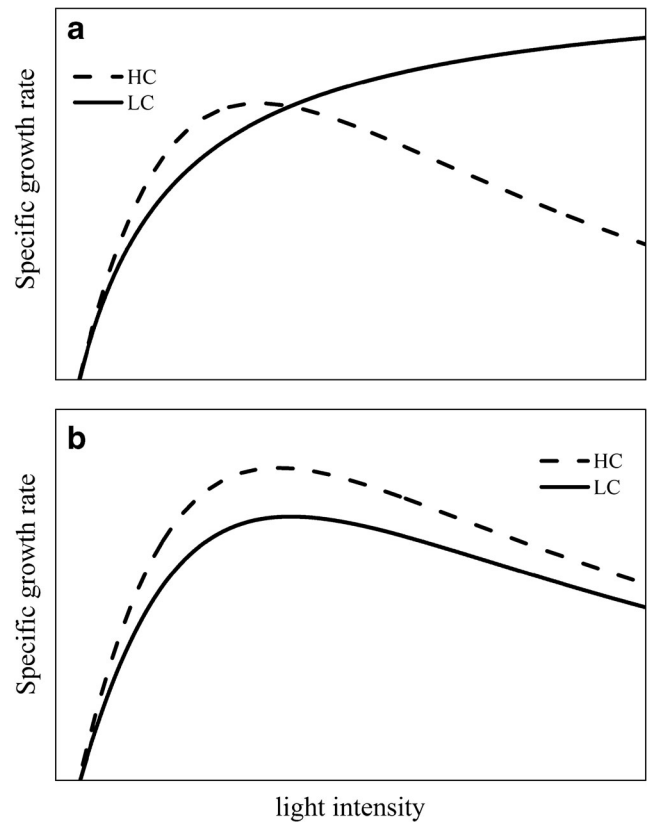
The decline of CO<sub>3</sub><sup>2-</sup> has an effect on the saturation ( $\Omega$ ) of CaCO<sub>3</sub> in seawater ( $\Omega = \text{Ca}^{2+} \times \text{CO}_3^{2-} / K_c$ ).  $K_c$  is the product of Ca<sup>2+</sup> × CO<sub>3</sub><sup>2-</sup> when CaCO<sub>3</sub> is saturated, which depends on the crystalline type of CaCO<sub>3</sub> (such as calcite and aragonite). Since the oceanic Ca<sup>2+</sup> concentration is relatively constant (approximately 10 mM), the CaCO<sub>3</sub> saturation mainly depends on the concentration of CO<sub>3</sub><sup>2-</sup>. In general, HCO<sub>3</sub><sup>-</sup> in the seawater accounts for more than 90% of the dissolved inorganic carbon (DIC), CO<sub>3</sub><sup>2-</sup> for about 9%, and CO<sub>2</sub> for less than 1% (these percentages change with temperature at different latitudes or regions) (Zeebe and Wolf-Gladrow 2001). Increasing atmospheric CO<sub>2</sub> concentrations result in an increase in dissolved CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, and H<sup>+</sup>, but a decrease in the concentration of CO<sub>3</sub><sup>2-</sup> and consequently a decrease in the saturation of CaCO<sub>3</sub>. Since the Industrial Revolution, the concentration of CO<sub>3</sub><sup>2-</sup> in the epipelagic seawater has decreased approximately by 10% (Orr et al. 2005). If the atmospheric CO<sub>2</sub> concentration doubles, the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in epipelagic seawater will also double, while the decline in CO<sub>3</sub><sup>2-</sup> concentration depends on temperature (latitudes) (Kleypas et al. 2006).

During the past 300 million years, atmospheric CO<sub>2</sub> concentrations have changed very slowly, allowing effective

mixing between the surface and deeper layers of the oceans, so that OA was moderate (Hönisch et al. 2012). Since the deposition of CO<sub>2</sub> into deeper oceanic layers takes thousands of years, OA would not disappear in the next few hundred years, even if anthropogenic emission stopped now abruptly (Raven et al. 2005).

OA modifies the oceanic carbonate chemistry (Millero 2007), which in turn affects organisms and ecosystems to different degrees in different waters and latitudes, considering compounded impacts with multiple environmental drivers (Riebesell and Gattuso 2015). Other key factors, such as exposure to solar radiation in the presence of UV radiation, temperature, and nutrient availability, also change, inevitably affect biological productivity and other ecological processes of marine ecosystems (Boyd 2011; Gattuso et al. 2015). The carbon chemistry in the oceans is of utter importance for photosynthetic organisms, including prokaryotic and eukaryotic phytoplankton as well as macroalgae and seagrasses, since these primary producers generate organic matter via photosynthesis that relies on the availability of inorganic carbon which changes with altered carbonate chemistry (Raymont 2014; Britton et al. 2016). The performance of the primary producers may have profound effects on secondary productivity and ecosystem services, such as food quality (Jin et al. 2015). Therefore, understanding the effects of OA on primary productivity is key to evaluating the functioning of marine ecosystems. At low dissolved inorganic carbon (DIC) levels in waters, increasing CO<sub>2</sub> concentrations usually augment growth and photosynthetic carbon fixation, while at high levels the increasing H<sup>+</sup> concentrations may impair these processes in many species. The dependence of phytoplankton physiological reactions on the DIC concentration and carbonate chemistry follows an optimum curve, as shown for the ecological important groups of coccolithophores, diatoms, and cyanobacteria (Miyairi 1995; Bach et al. 2015; Liu et al. 2017).

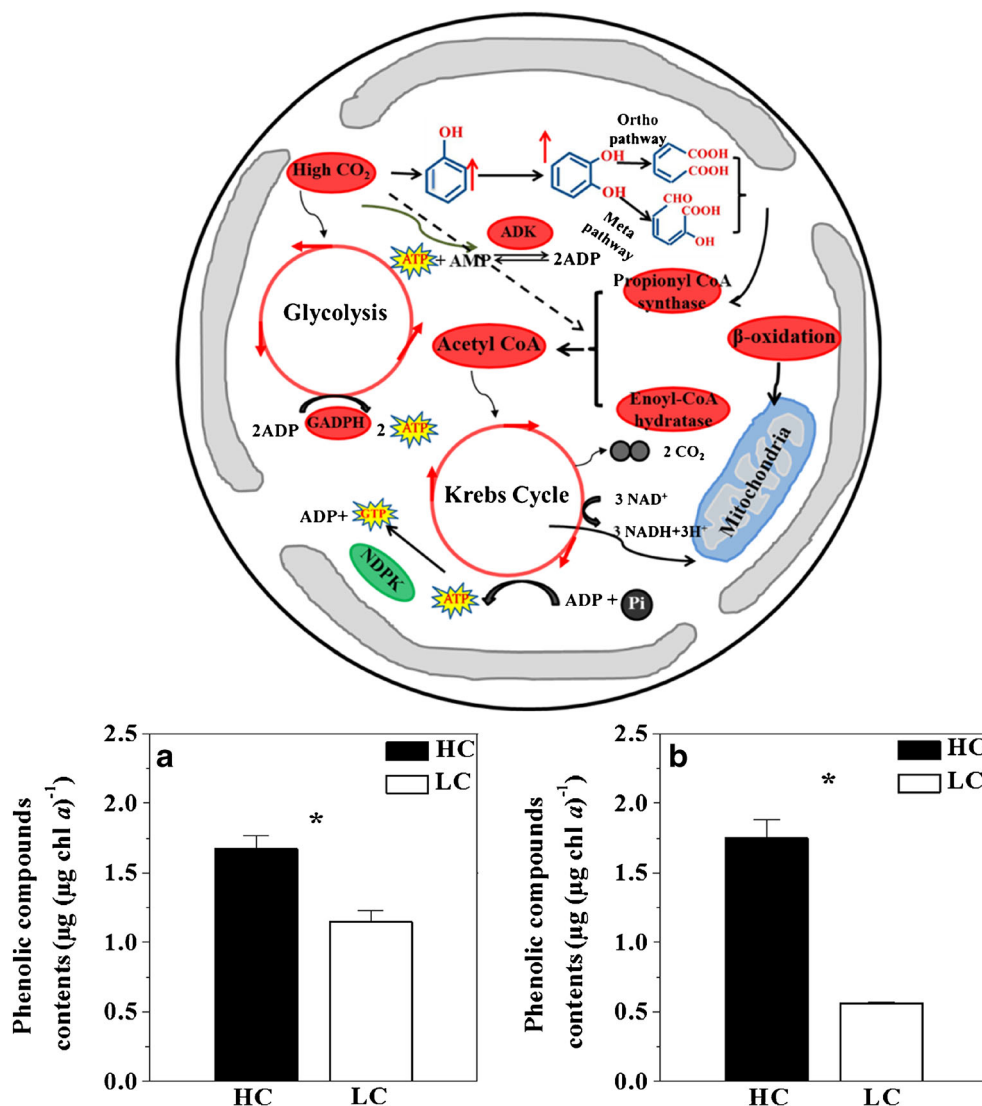
Recent studies have indicated that OA may either enhance photosynthesis and growth in phytoplankton (Riebesell and Tortell 2011) or have no significant effect (Tortell et al. 2000; Kim 2006; Gao and Campbell 2014) or may even decrease productivity by enhancing mitochondrial respiration and photorespiration (Wu et al. 2010; Gao et al. 2012a; Mackey et al. 2015). When the effect of OA is considered together with high PAR, previous studies have shown that it decreases carbon fixation in phytoplankton communities and impairs growth of diatoms at high PAR levels, but has the opposite (stimulating) effect on diatoms at low PAR levels (Gao et al. 2012b) (Fig. 1a). These puzzling results can be explained by the fact that high CO<sub>2</sub> concentrations downregulate the uptake capacity of the cells for DIC (CO<sub>2</sub> concentrating mechanisms), so that energy, which is used for the active uptake mechanism, is saved and phytoplankton growth at low irradiances is augmented. Being consistent with the results of Gao et al. (2012b), at high light intensities, OA decreased the maximal growth rates of the



**Fig. 1** Concepts of modulation effect of rising CO<sub>2</sub> on the light response curves of growth rates of diatoms (a) and the coccolithophore *Emiliana huxleyi* (b). At low PAR, rising CO<sub>2</sub> levels augment growth rates of diatoms, while at high PAR rising CO<sub>2</sub> impairs them (a). At low and high PAR, rising CO<sub>2</sub> level augments growth rates of coccolithophore *E. huxleyi* (b). Conceptual figure was based on the data of Gao et al. (2012b) and Jin et al. (2017). LC indicates phytoplankton grew at current CO<sub>2</sub> level and HC indicates phytoplankton grew at the CO<sub>2</sub> level at the end of this century

coccolithophore *Gephyrocapsa oceanica* (Zhang et al. 2015). However, OA was reported to increase the growth rates of the coccolithophore *Emiliana huxleyi* at both low and high light intensities (Jin et al. 2017) (Fig. 1b). This indicates that *E. huxleyi* may have a potential to dissipate more energy even under OA due to extra energy cost of calcification and the maintaining of the cell homeostasis, displaying a different response from that of the diatoms. Phytoplankton species, as reported in diatoms and coccolithophores, increase synthesis and accumulation of toxic phenolics under OA conditions, and their degradation is suggested to generate additional energy against the acidic stress, as shown in increased mitochondrial respiration (Jin et al. 2015). By this mechanism, OA enhances several biochemical pathways including  $\beta$ -oxidation of lipids, the tricarboxylic acid (TCA) cycle, and glycolysis (Fig. 2) (Jin et al. 2015). In addition, toxin biosynthesis is linked to the autotrophic metabolism of some harmful algal blooms (HAB). Changes in CO<sub>2</sub> availability and temperature may indirectly affect cellular toxicity (Fu et al. 2012). OA may increase the production of toxins in harmful bloom-forming algae

**Fig. 2** Upper panel: Ocean acidification (OA) upregulates (red) or downregulates (green) metabolic pathways of calcified phytoplankton *E. huxleyi*. The cells upregulate several metabolic pathways such as  $\beta$ -oxidation, the TCA cycle, and glycolysis (upper panel) which is required for the degradation of phenolics, in order to gain more energy to resist OA. Lower panel: OA significantly increased the concentrations of phenolics of phytoplankton assemblages in 30-L microcosm (left panel) and in 4000-L mesocosm experiments (right panel). LC indicates phytoplankton grew at 395  $\mu\text{atm CO}_2$ , and HC indicates phytoplankton grew at 1000  $\mu\text{atm CO}_2$  (Jin et al. 2015). Vertical lines represent standard deviation of the means. \*Significance at the  $p < 0.05$  level



as has been shown in the diatom *Pseudo-nitzschia* (Sun et al. 2011) and in toxic dinoflagellates *Alexandrium fundyense* (Hattenrath-Lehmann et al. 2015). van Wells et al. (2015) suggested that phytoplankton toxins account for a very small proportion of total cellular carbon, and there is no evidence that cellular toxicity is directly related to the intra- or extracellular pH. However, slight differences in culture conditions may affect the trends in toxin production. In addition, OA increased the transparent exopolymer particle (TEP) concentrations during an algal bloom in the Baltic Sea during spring 2009 (Engel et al. 2014). This implies that rising  $\text{CO}_2$  supports production and exudation of carbon-rich components and enhances particle aggregation and settling. At a low  $\text{CO}_2$  level, the abundance of *Phaeocystis* increased by about 60% in the Peruvian coast, which resulted in higher nitrate/silicate (N/Si) consumption ratios, while at high  $\text{CO}_2$  level, the abundance of diatom increased by 50%, which increased the N/Si consumption (Tortell et al. 2002; Domingues et al. 2017). Elevated  $\text{CO}_2$

concentration increased DIC consumption of a natural plankton community in Raunefjorden, Norway, whereas nutrient uptake remained the same (Riebesell et al. 2007). From a mesocosm experiment, Larsen et al. (2008) reported that the abundance of the virus, EhV, decreased with rising  $\text{CO}_2$  levels, whereas its host, *E. huxleyi*, showed the reverse opposite response with a slight increase in the abundance at higher  $\text{CO}_2$ . This suggests that the reduced viral concentration was caused by changes in host-virus interaction rather than being a secondary effect of a reduced algal production. On the other hand, Chen et al. (2015) found that OA treatment and virus infection acted synergistically to enhance photoinhibition and reduce carbon fixation in *Phaeocystis globosa*.

Cyanobacterial nitrogen fixation can provide biologically usable nitrogen in oligotrophic waters, which promotes growth of phytoplankton and increases photosynthetic carbon fixation (Eichner et al. 2014). By this mechanism, nitrogen-fixing cyanobacteria (diazotrophs) indirectly mitigate global

warming (Michaels et al. 2001; Berthelot et al. 2015). In cyanobacteria with heterocysts, OA can either augment (Wannicke et al. 2012) or impair (Czerny et al. 2009) nitrogen fixation. In cyanobacteria without heterocysts, the response of nitrogen fixation to OA varies between species (Eichner et al. 2014). In *Trichodesmium* and several cyanobacteria groups, OA slows nitrogen fixation and growth (Shi et al. 2012), while in other species no or little effects were reported (Böttjer et al. 2014; Gradoville et al. 2014). However, enhanced nitrogen fixation rate has been shown in *Trichodesmium* after having been adapted to OA for hundreds of generations. Adapted *Trichodesmium* displayed shifts in diel nitrogen fixation patterns, and increased activity of a potentially regulatory DNA methyltransferase (Hutchins et al. 2015). These contradictory results may be due to species- or strain-specific physiological response to rising CO<sub>2</sub>, or different experimental culture conditions such as short- and long-term growth under the effect of OA. Because of these differences, biodiversity and community structure of phytoplankton will change with rising CO<sub>2</sub> (Hutchins et al. 2013; Gradoville et al. 2014). In a freshwater cyanobacterium, for example, Van de Waal et al. (2011) showed that, within mixtures of toxic and non-toxic strains of *Microcystis aeruginosa*, the toxic strain became dominant in competition at low CO<sub>2</sub> levels. In marine ecosystems, species-specific responses in photosynthetic organisms and their grazers to OA may result in significant differences in phytoplankton community structures.

Phytoplankton species are affected by OA both in pelagic and coastal waters. However, in pelagic waters under limitation of dissolved inorganic macronutrients or less mixing, phytoplankton cells may respond differentially than coastal species, as reported for diatoms (Li et al. 2016). While most of the earlier investigations on this topic have been carried out in the laboratory under controlled conditions, it is mandatory to study the effects of OA on photosynthesis and growth of phytoplankton under natural conditions in order to evaluate the influence of multiple environmental factors on phytoplankton (Riebesell and Gattuso 2015; Tilstone et al. 2016; Grear et al. 2017).

## Ocean warming and its effect on phytoplankton

During the last three decades the surface temperature on Earth has increased continuously and faster than any preceding period since the beginning of the Industrial Revolution (Hansen et al. 2006). IPCC estimates that surface ocean temperatures will increase by about 1 °C (RCP2.6) to 3 °C (RCP8.5) by the end of the century (IPCC 2014).

Enzymatic efficiency, photosynthetic carbon incorporation, and other metabolic activity are controlled by the ambient temperatures (Beardall and Raven 2004). The resulting growth rate can be defined by thermal performance curves (TPC). These

curves show an initial increase with increasing temperatures up to an optimum value and then a sharp decline towards the upper limit of the permissive temperature window (Huey and Stevenson 1979). Experimentally, TPCs are recorded by measuring the response rate at 5–7 fixed temperatures and they can be modeled mathematically (Boyd et al. 2013). These models describe the optimal temperature, the width of the permissive thermal window and the maximal rate of a response, or the overall rate across all temperatures (Zhang et al. 2014). However, the width or rates in TPCs are affected by other environmental forcings such as CO<sub>2</sub> levels and copper concentration (Listmann et al. 2016; Leung et al. 2017).

The optimal growth rate temperatures varied from 30 to 35 °C for four *Skeletonema menselii* and five *Skeletonema ardens* strains (Table 1). The optimal growth temperature was very close to the upper limit of a large temperature window in eight diatom species isolated from temperate regions to the Arctic (Suzuki and Takahashi 1995). This optimal growth temperature is generally higher than the ambient temperature where the organisms were isolated. Kaeriyama et al. (2011) reported significant differences between strains of seven *Skeletonema* species when measuring growth rates at temperatures in the range from 10 to 40 °C. Growth rates of 11 *E. huxleyi* strains were determined in the range from 8 to 28 °C; each strain had a specific temperature window and optimum related to their original niche (Zhang et al. 2014). Minimum growth temperature was closely related to the biogeography of five coccolithophorid species when the growth rate was studied in the range between 6 and 25 °C (Buitenhuis et al. 2008). Growth at 15 °C and 26.3 °C, respectively, for 2.5 years, showed that the optimum growth temperature of *E. huxleyi* isolated from Norwegian coastal waters was 0.7 °C higher for the strain grown at 26.3 °C than that grown at 15 °C (Listmann et al. 2016). The maximum permissive temperature was 1 to 3 °C higher in the strain grown at the elevated temperature.

In summary, these results indicate that differences in optimum temperature, maximum value, and width of the thermal window for growth rates may be due to species or strain characteristics, different provenance as well as different culture conditions such as light intensity or dissolved inorganic macronutrient concentrations (Boyd et al. 2013). These studies showed that phytoplankton species isolated from temperate or polar waters usually have a lower optimal temperature and a broader permissive temperature window than those isolated from tropical waters. Phytoplankton isolated from cool waters has usually optimum growth temperatures which are much higher than the ambient temperature at their growth habitat while those from warm waters reveal optima close to the ambient water temperature (Thomas et al. 2012).

Ocean warming is most significant in polar regions (Hansen et al. 2006), and changes in temperature could directly affect local microzooplankton species composition, abundances, and growth efficiencies. Rose et al. (2009)

**Table 1** Summary of variations in optimal temperature ( $T_{opt}$ ), maximal growth rate ( $\mu_{max}$ ), and temperature niche width ( $w$ ) of phytoplankton isolated from various environments. NS indicates no source was found

Species/strain	Habitat	In situ temp. (°C)	$T_{opt}$ (°C)	$\mu_{max}$ (day <sup>-1</sup> )	$w$ (°C)	Incubation irradiance (μmol photons m <sup>-2</sup> s <sup>-1</sup> )	Reference
<i>Asterionella formosa</i>	36° N, 140° E	8	20	1.3	2–30	200	(Suzuki and Takahashi 1995)
<i>Chaetoceros pseudocurvisetus</i>	35° N, 139° E	25	25	1.6	15–35	200	(Suzuki and Takahashi 1995)
<i>Nitzschia frigida</i>	75° N, 95° W	-1.8	2	0.4	-1.8–5	100	(Suzuki and Takahashi 1995)
<i>Skeletonema costatum</i>	36° N, 140° E	15	25	1.5	2–35	200	(Suzuki and Takahashi 1995)
<i>Thalassiosira nordenskioeldii</i>	44° N, 144° E	-1.8	15	1.0	-1.8–20	100	(Suzuki and Takahashi 1995)
<i>Ditylum brightwellii</i>	NS	NS	20	0.7	NS	50	(Montagnes and Franklin 2001)
<i>Phaeodactylum tricornutum</i>	NS	NS	20	1.0	NS	50	(Montagnes and Franklin 2001)
<i>S. costatum</i>	NS	NS	20	0.9	NS	50	(Montagnes and Franklin 2001)
<i>T. pseudonana</i>	NS	NS	25	1.4	5–32	130	(Claquin et al. 2008)
<i>S. marinoi</i>	NS	NS	23	1.2	0–31	130	(Claquin et al. 2008)
<i>Pseudo-nitzschia fraudulentula</i>	NS	NS	21	0.8	5–24	130	(Claquin et al. 2008)
<i>S. ardens</i>	33° N, 130° E	28	35	2.3	10–40	150	(Kaeriyama et al. 2011)
<i>S. costatum</i>	33° N, 130° E	20	30	1.3	10–35	150	(Kaeriyama et al. 2011)
<i>S. marinoi-dohrnii</i>	33° N, 130° E	12	30	1.7	5–35	150	(Kaeriyama et al. 2011)
<i>S. japonicum</i>	33° N, 130° E	25	25	1.6	5–30	150 <sup>1</sup>	(Kaeriyama et al. 2011)
<i>S. menzeli</i>	33° N, 130° E	28	30	2.6	10–40	150	(Kaeriyama et al. 2011)
<i>S. tropicum</i>	33° N, 130° E	20	25	1.6	10–35	150	(Kaeriyama et al. 2011)
<i>T. pseudonana</i> CCMP 1011	18° N, 65° E	NS	25	1.1	6–32.5	Saturating light levels	(Boyd et al. 2013)
<i>T. pseudonana</i> CCMP 1012	32° N, 116° W	NS	25	1.3	6–32.5	Saturating light levels	(Boyd et al. 2013)
<i>T. pseudonana</i> CCMP 1013	53° N, 4° W	NS	25	1.4	6–35	Saturating light levels	(Boyd et al. 2013)
<i>T. pseudonana</i> CCMP 1014	28° N, 155° E	NS	25	1.4	6–35	Saturating light levels	(Boyd et al. 2013)
<i>T. pseudonana</i> CCMP 1015	49° N, 123° E	NS	25	1.4	6–35	Saturating light levels	(Boyd et al. 2013)
<i>T. pseudonana</i> CCMP 1335	41° N, 73° E	NS	30	1.4	6–35	Saturating light levels	(Boyd et al. 2013)
<i>Trichodesmium erythraeum</i> KO4–20	15° S, 155° E	NS	28	0.3	16–35	Saturating light levels	(Boyd et al. 2013)
<i>T. erythraeum</i> 2175	7° N, 49° W	NS	26	0.3	18–35	Saturating light levels	(Boyd et al. 2013)
<i>Crocospaera watsonii</i> WH 3A	7° N, 49° W	NS	28	0.3	22–35	Saturating light levels	(Boyd et al. 2013)
<i>C. watsonii</i> WH84	11° S, 32° W	NS	28	0.4	22–35	Saturating light levels	(Boyd et al. 2013)
<i>C. watsonii</i> WH0005	21° N, 157° W	NS	28	0.4	22–35	Saturating light levels	(Boyd et al. 2013)
<i>T. pseudonana</i>	NS	NS	25	1.3	NS	NS	(Leung et al. 2017)
<i>Emiliania huxleyi</i> B92/21	60° N, 5° E	NS	18	1.3	NS	100	(Conte et al. 1998)
<i>E. huxleyi</i> G1779Ga	60° N, 20° W	NS	21	1.7	NS	100	(Conte et al. 1998)

**Table 1** (continued)

Species/strain	Habitat	In situ temp. (°C)	$T_{opt}$ (°C)	$\mu_{max}$ (day <sup>-1</sup> )	w (°C)	Incubation irradiance (μmol photons m <sup>-2</sup> s <sup>-1</sup> )	Reference
<i>E. huxleyi</i> M181	32° N, 62° W	NS	24	1.5	NS	100	(Conte et al. 1998)
<i>E. huxleyi</i> S. Africa	29° S, 31° E	NS	24	1.3	NS	100	(Conte et al. 1998)
<i>E. huxleyi</i> Van556	49° N, 144° W	NS	18	1.1	NS	100	(Conte et al. 1998)
<i>Gephyrocapsa oceanica</i> AB1	36° S, 174° E	NS	24	1.3	NS	100	(Conte et al. 1998)
<i>E. huxleyi</i> TQ26DIP	NS	NS	20	1.4	4–30	180	(Buitenhuis et al. 2008)
<i>G. oceanica</i> NS6–2	NS	NS	25	0.9	NS	180	(Buitenhuis et al. 2008)
<i>Calcidiscus leptoporus</i> NS10–2	NS	NS	12	0.6	9–25	180	(Buitenhuis et al. 2008)
<i>C. leptoporus</i> N482–1	NS	NS	20	0.4	9–25	180	(Buitenhuis et al. 2008)
<i>Coccolithus braarudii</i> N476–2	NS	NS	15	0.4	9–25	180	(Buitenhuis et al. 2008)
<i>E. huxleyi</i> M23	38° N, 28° W	17	24	1.6	4–30	160	(Zhang et al. 2014)
<i>E. huxleyi</i> M22	38° N, 28° W	17	24	1.6	4–30	160	(Zhang et al. 2014)
<i>E. huxleyi</i> M21	38° N, 28° W	17	24	1.6	4–30	160	(Zhang et al. 2014)
<i>E. huxleyi</i> M19	38° N, 28° W	17	23	1.6	4–30	160	(Zhang et al. 2014)
<i>E. huxleyi</i> M13	38° N, 28° W	17	25	1.5	4–30	160	(Zhang et al. 2014)
<i>E. huxleyi</i> M10	38° N, 28° W	17	24	1.6	4–30	160	(Zhang et al. 2014)
<i>E. huxleyi</i> 85	60° N, 5° E	10	23	1.6	4–28	160	(Zhang et al. 2014)
<i>E. huxleyi</i> 63	60° N, 5° E	10	23	1.6	4–28	160	(Zhang et al. 2014)
<i>E. huxleyi</i> 62	60° N, 5° E	10	23	1.7	4–28	160	(Zhang et al. 2014)
<i>E. huxleyi</i> 41	60° N, 5° E	10	23	1.8	4–28	160	(Zhang et al. 2014)
<i>E. huxleyi</i> 17	60° N, 5° E	10	23	1.6	4–28	160	(Zhang et al. 2014)
<i>E. huxleyi</i> RCC1710	34° N, 129° E	NS	25	1.2	6–30	300	(Rosas-Navarro et al. 2016)
<i>E. huxleyi</i> RCC1252	41° N, 140° E	NS	25	1.2	6–30	300	(Rosas-Navarro et al. 2016)
<i>E. huxleyi</i> IAN01	NS	NS	25	1.3	6–30	300	(Rosas-Navarro et al. 2016)

NS no source was found

observed that microzooplankton abundance increased by 43% in a Ross Sea plankton community incubated for 1 week at 4 °C above the local ambient temperature. In addition, in a mesocosm experiment, warming showed a larger positive effect on heterotrophic processes than on the phototrophic process, implying less energy and material transfer to higher trophic levels. Edward and Richardson (2004) reported that ocean warming has shifted the seasonal cycles of growth and reproduction of some copepods to earlier in the year, which cause a loss of the trophic transfer of primary productivity to higher trophic levels.

Although temperature has a strong influence on phytoplankton community composition, it is unlikely to drive competitive selection of HAB species over non-HAB species alone (van Wells et al. 2015). Increased temperature decreased growth rates of the diatom *Cylindrotheca closterium*, but increased the biomass of small chlorophytes in a reef lagoon in the Mexican Caribbean (Halac et al. 2013). Groetsch et al. (2016) showed that nutrient reduction led to decreasing spring bloom intensity in the Baltic Sea during 2000–2014, while increased levels of water temperature, solar radiation, and reduced wind speed were associated with a lengthening bloom period. Mapping of diatoms, dinoflagellates, and copepods in the NE Atlantic and North Sea from 1954 to 2013 showed that dinoflagellates and copepods migrated fast poleward, which tended to track the rate of isotherm movement, while the range of the diatoms changed slowly (Chivers et al. 2017). This result has major implications for the biological assemblages. Using satellite-monitored chlorophyll *a* (Chl *a*) imaging during 1998–2014, Marchese et al. (2017) showed that phytoplankton blooms lasted longer under conditions of the protracted open water period in North Water polynya, whereas during years with a persistent ice cover, blooms were of shorter duration. The decline in Chl *a* could be related to large-scale changes in the Arctic Ocean such as increased surface temperature and freshwater content (Marchese et al. 2017). Satellite records have shown long-term decreases in globally integrated marine phytoplankton biomass and primary production linked to global warming (Siegel et al. 2013). This was also confirmed by current observations and century-long in situ monitoring of water transparency (Boyce et al. 2010) and coupled to carbon-climate models (Steinacher et al. 2010). Different results from different regions and over different time scales as well as controversial interpretations of satellite observations indicate uncertainties on predicted responses of marine phytoplankton community composition to ocean warming (Chavez et al. 2011; Siegel et al. 2013; Henson et al. 2016).

### Effects of UV radiation on phytoplankton productivity

Anthropogenically produced and emitted chlorinated fluorocarbons (CFCs) and chlorinated organic compounds have

been reported to catalytically destroy ozone in the stratosphere since the 1970s (Staehelin et al. 2001). As a consequence, developments of the Antarctica and the Arctic ozone holes resulted in increasing UV-B irradiances on the ground (Stolarski 1988; Manney et al. 2011). Also, at mid-latitudes, ozone depletion and resulting higher UV-B levels were found while the originally high UV-B levels in the tropics did not increase further (Bais et al. 2015). Due to the enforcement of the Montreal Protocol and its amendments, the concentrations of most of the human being-made chemicals that led to ozone depletion are declining. However, the ozone layer has not yet recovered due to the long lifetimes of the ozone-depleting substances on the order of many decades (Hoffmann et al. 2014) and consequentially the elevated UV-B levels are predicted to only slowly decrease (Bais et al. 2015). Nevertheless, stratospheric cooling and the possible strengthening of the Brewer-Dobson circulation (BDC) among other factors may even result in a super-recovery of Antarctic ozone layer around mid-century (Solomon et al. 2016). This is because strengthened BDC would result in a faster removal of CFCs from the atmosphere and lead to a redistribution of ozone in the lower stratosphere from the tropics to the mid-latitudes which reduces column ozone in the tropics and increases it in mid-latitudes (Rind et al. 1990). On the other hand, cell exposures to solar UV-B radiation are suggested to increase due to enhanced stratification of the upper mixed layer (UML) in the oceans (Gao et al. 2012b), which is associated with global warming. Thinner UML exposes phytoplankton dwelling in this layer to higher levels of visible and UV radiation. At the same time, increased stratification hinders the transport of nutrients from deeper waters through the thermocline into the UML, negatively affecting phytoplankton growth and productivity (Boyce et al. 2010). Therefore, increased attention should be given to the UV-B exposure and other environmental global change drivers such as dissolved inorganic macronutrient (Häder and Gao 2015; Häder et al. 2015).

Particulate organic matter (POM) and chromophoric dissolved organic matter (CDOM) are mainly responsible for the attenuation of PAR in estuary and coastal ecosystems (Steinberg et al. 2004). Dissolved organic carbon (DOC) and particulate organic carbon (POC) are the main absorbers of UV-A and UV-B, respectively. Open ocean waters have a higher transparency and the attenuation mainly depends on the low biomass density and their degradation products as well as the excretion of inorganic and organic matter of zooplankton (Steinberg et al. 2004).

The photic zone is defined by the penetration (depth of 1% surface level) of visible radiation into water columns. Depending on the load of dissolved and particulate matter, penetration of PAR varies greatly between marine ecosystems, e.g., in the Atlantic, UV-B (310 nm) can reach 30 m, UV-A (380 nm) 100 m, blue light (450–500 nm) over 190 m, and other visible light wavelengths (600–700 nm) 20 m (Piazena



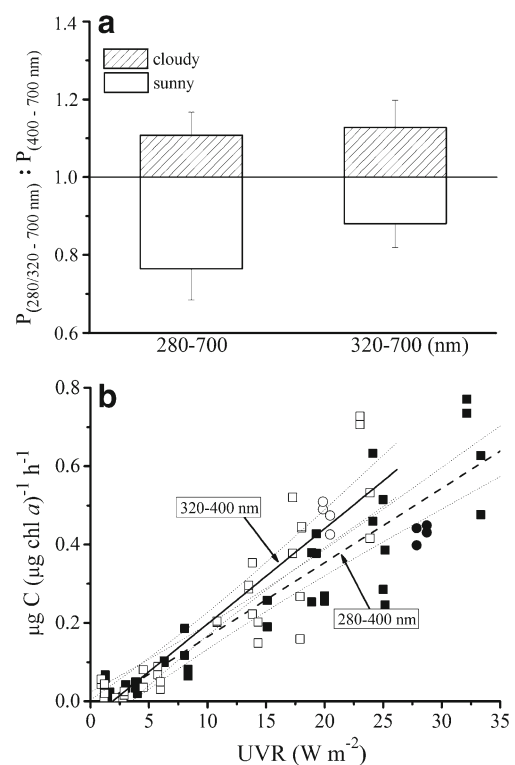
et al. 2002). In open ocean waters of the South China Sea, the visible light can penetrate > 80 m, UV-A 50 m and UV-B 38 m which accounts for 62 and 47% of the depth of the euphotic zone, respectively (Li et al. 2009). Coastal waters are characterized by high concentrations of absorbing substances, e.g., off the coast of Shantou, visible light penetrates less than 10 m into the waters adjacent to an aquaculture area; UV-A and UV-B transmit less than 5 and 3 m, respectively, accounting for 50 and 30% of the depth of the euphotic zone (Gao et al. 2007; Li and Gao 2012).

Global climate change will have an impact on the UV transmission in the oceans (United Nations Environment Programme Environmental Effects Assessment Panel 2017). Increasing temperatures will augment bacterial decay and photodegradation of CDOM and thus increase the penetration of UV into the water column (Hansell and Carlson 2014). However, vertical mixing of phytoplankton above the thermocline due to wind and waves results in variable exposure to PAR (Gargett and Marra 2002; Neale et al. 2003). Characteristics of photoacclimation are a reduction in pigment content and effective photochemical quantum yield ( $F'_v/F'_m$ ) (Geider et al. 1997; Gao et al. 2012b). It was shown that the photoacclimation response is an important component of temporal Chl variability across the global ocean, and light-driven decrease in Chl can be associated with an increased surface layer photosynthesis due to shallowing of the UML (Behrenfeld et al. 2016). UV-B irradiances at the Earth surface change with latitude, total column ozone, and attenuation in the atmosphere. This is further modulated by water attenuation and depth for aquatic organisms. This variability needs to be taken into account when studying the effects of UV-B radiation in the natural environment (see reviews by Häder and Gao 2015; Häder et al. 2015).

One of the targets of UV-B radiation is the DNA in phytoplankton (Häder and Gao 2015; Meador et al. 2009), and this radiation also inhibits the repair of the damage (Rastogi et al. 2014). In addition to many other direct damages, UV can induce free oxygen radicals which inflict oxidative stress to the cells (Häder and Gao 2015). This can affect photosynthetic pigments and decrease biomass production and growth. For example, enhanced UV exposures decreased growth rates of diatoms while increased growth rates of cryptophytes in the Ria Formosa coastal lagoon, southern coast of Portugal (Domingues et al. 2017). UV-B accounts for less than 1% of the total PAR at the Earth surface, while UV-A accounts for about 6–8%. However, in most cases, UV-B inflicts much stronger damage than radiation at longer wavelengths. The damage by PAR is dependent of the previous light history of communities (Häder et al. 2014), and the mixing velocity (Villafañe et al. 2007). PAR is an indispensable prerequisite for photosynthesis, but at the same time the organisms are exposed to detrimental UV. Because of the constant exposure to UVR, phytoplankton have developed mechanisms to mitigate UV-inflicted damage during their long evolution. UV-

mitigating strategies include the production of UV-screening compounds such as scytonemin and mycosporine-like amino acids (MAAs), vertical migration, and crust formation (Moisan et al. 2009). In addition, free radicals are being removed by several mechanisms such as enzymatic and non-enzymatic quenching of reactive oxygen species (ROS) (Häder et al. 2015; Richa et al. 2016). These mitigating strategies can differ in different species; therefore, UV radiation is an important driver for species competition (Zhang et al. 2013).

In the surface layer, phytoplankton are exposed to excessive visible and UV radiation which decreases productivity (Häder et al. 2015), but at low irradiances, e.g., on cloudy days, UV-A radiation may even contribute to photosynthetic carbon fixation in marine phytoplankton (Fig. 3a) (Gao et al. 2007). This was confirmed by experiments with a diatom-dominated phytoplankton community in which visible light was filtered out: photosynthetic carbon fixation increased with increasing UV-A irradiances. In contrast, the presence of UV-B reduced carbon incorporation (Fig. 3b). Large-celled phytoplankton species are better equipped to utilize UV-A for photosynthetic carbon fixation than smaller ones (Li et al.



**Fig. 3** a Photosynthetic carbon fixation rates of phytoplankton assemblages under PAR + UV-A + UV-B or PAR + UV-A as compared to those under only PAR in different weather conditions (a). b The carbon fixation rate of coastal phytoplankton assemblages of the South China Sea exposed to solar UVR (280–400 nm, black symbols) or UV-A (320–400 nm, white symbols). The solid and dashed lines represent a linear fit of the data ( $p < 0.0001$ ), while the dotted lines are the 95% confidence limit (Gao et al. 2007)

2011; Li and Gao 2013). UVR also affects nutrient uptake in phytoplankton. Under phosphate-sufficient condition in La Caldera, Sierra Nevada, Spain, UVR increased the uptake of phosphate or stimulated the activity of alkaline phosphatase of phytoplankton, which resulted in low C/P ratio and decrease in Chl *a* concentration (Villar-Argaiz et al. 2017). Under five different N/P ratios, Guan and Li (2017) showed that the Redfield ratio of 16:1 is optimal for the growth and phosphorylation of the dinoflagellate *Karenia mikimotoi*.

### Combined effects of ecological stress factors

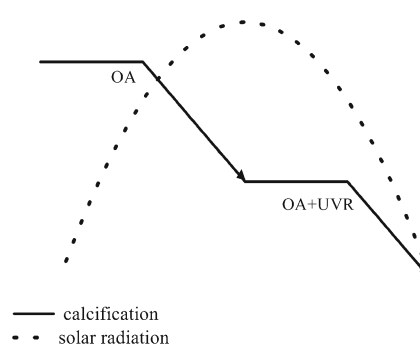
Phytoplankton in the oceanic UML is exposed to the pressure of environmental stress factors such as increasing OA, rising temperatures, and enhanced exposures to UVR. While there is a large body of publications on the individual effects of these environmental drivers, it is difficult to predict the trends in biological carbon fixation and the efficiency of the biological pump due to the lack of data related to effects of multiple global change drivers (Beardall et al. 2014; Riebesell and Gattuso 2015).

The photosynthetic apparatus of phytoplankton reacts to excessive UVR within a short time on the order of minutes. The combined effects of OA and UVR (280–400 nm) significantly reduce the photochemical efficiency ( $Y'$ ) of photosystem II (PSII) in the diatom *Cylindrotheca closterium* f. *minutissima* grown at 1000  $\mu\text{atm}$   $\text{CO}_2$  under PAR (Wu et al. 2012). Even after an acclimation to these conditions for 9 days, the coupled stress of OA and UV significantly decreased the electron transport rate; however, there was no significant difference in growth. *Phaeocystis globosa* grown at 1000  $\mu\text{atm}$   $\text{CO}_2$  (with adjusted pH) under PAR showed a negative correlation of the photochemical efficiency with the irradiance of PAR (with the lowest values at noon), and there was a coupling effect of UV and OA on the photochemical efficiency (Chen and Gao 2011). This species increased its photochemical efficiency and decreased its non-photochemical quenching (NPQ) on cloudy days under OA, but on sunny days OA did not affect the  $Y'$  significantly with increased NPQ (Chen and Gao 2011). Under fluctuating PAR, OA counteracted the increase in photosynthetic carbon fixation caused by UV-A and the inhibition by UV-B decreased (Jin et al. 2013). At low PAR, combined OA and UVR treatments decreased the POC production rate in *E. huxleyi*, while at higher irradiances the combined stress factors increased the POC production rate (Xu and Gao 2015). Increased levels of PAR counteracted the negative effects of OA on calcification of *E. huxleyi* (Jin et al. 2017). In addition, OA was reported to counteract the negative effects of UVR on diatoms. It was suggested that inconsistencies in phytoplankton responses to OA and UVR may be related to factors such as high degree of inter- and even intraspecific variability, different levels of pre-

acclimation to experimental conditions, and different initial algal assemblages (Domingues et al. 2017).

OA and UVR have a synergistic negative effect on calcareous algae. OA decreases the calcification in coccolithophorids and coralline algae and thins the protective calcified layer. As a result, the increased UVR transmission worsens the damage inflicted by UVR and impairs their cellular functions (Gao et al. 2009; Gao and Zheng 2010; Xu et al. 2014) (Fig. 4). Coralline algae enhanced production of UV-screening pigments (mainly MAAs) when exposed to UVR with flow-through seawater (Gao and Zheng 2010).

Combined effects of OA and warming are usually studied with two levels of each variable tested. Using 20 and 24 °C as well as 385 and 750  $\mu\text{atm}$  indicated that OA and warming synergistically augmented growth rates in eight *Skeletonema marinoi* strains isolated from the North Sea (Kremp et al. 2012). But in similar experiments with eight *S. marinoi* strains from the Adriatic Sea, neither OA nor warming or their combination enhanced the growth rates. This may be due to the large genetic diversity within the Adriatic Sea population. Hyun et al. (2014) observed that rising temperature induced different effects on growth rates of *Skeletonema costatum*, *Chaetoceros debilis*, *Thalassiosira nordenskioeldii*, and *Chaetoceros didymus*. Whereas, neither OA conditions alone nor in combination with ocean warming significantly augmented growth rates in these four species. In the coccolithophore *E. huxleyi* growth rate decreased when the temperature was raised from 15 to 26.3 °C, and the decrease was larger at 1100  $\mu\text{atm}$  than at 400  $\mu\text{atm}$  (Schlüter et al. 2014). After adaptation to 26.3 °C for 1 year (460 asexual generations), growth rates as well as POC and particular inorganic carbon (PIC) production in the same species increased by 20, 52, and 101%, respectively, when *E. huxleyi* was exposed to 26.3 °C and 2200  $\mu\text{atm}$  compared to the non-adapted culture. Coccolithophores have developed a calcified exoskeleton as protection against grazing pressure, viral and bacterial attack (Monteiro et al. 2016), and UVR (Gao et al. 2009). Obviously, this energy-expensive strategy has been successful



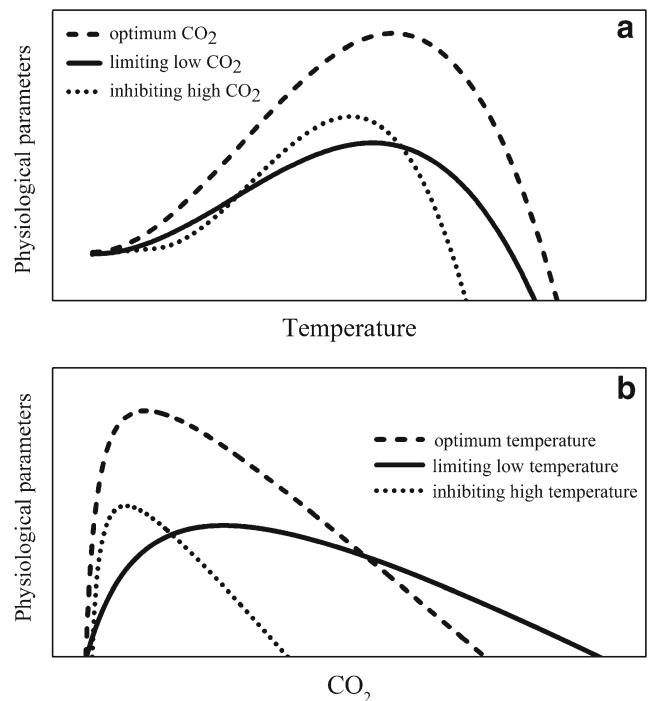
**Fig. 4** Synergistical negative effects of OA and UV on calcification. The carbon fixation in calcified algae decreases when affected by OA. The compounding effect of OA and UV further lowers the calcification (Gao et al. 2009; Xu et al. 2014)

as shown by their wide distribution and large biomass production in the oceans. A recent study showed that increased temperatures add to the negative effects of OA on *E. huxleyi* morphology (Milner et al. 2016).

In other phytoplankton groups and communities in Arctic open waters, chlorophyll *a* concentration and primary production decreased when the temperature was raised from 1 to 6 or 10 °C in laboratory cultures (Coello-Camba et al. 2014). In addition, OA slightly increased the primary production at 1 and 6 °C. At 1 °C, the phytoplankton communities were dominated by large centric diatoms (11 µm in diameter), and the communities successively became dominated by small phytoplankton (4-µm centric diatoms and 5.9-µm flagellates) at 10 °C. In agreement with the results of Coello-Camba et al. (2014), examination of in situ data revealed that at 1 and 6 °C, rising CO<sub>2</sub> concentration enhanced the gross primary production of the Arctic Ocean (Barents-Greenland Sea/Fram Strait) (Holding et al. 2015). Synergistic negative effects of UVR and temperature were only detected at the species level in large diatoms and in large cryptophytes in a reef lagoon (Halac et al. 2013). In a phytoplankton community in the Kiel Fjord, the structure changed when the temperature was increased from 16.5 to 22.5 °C (Paul et al. 2016): zooplankton abundance increased and consequently their food availability (phytoplankton species such as *Teleaulax* sp. *Prorocentrum micans*, *Heterocapsa triquetra*, and *Ditylum brightwellii*) decreased. At 16.5 °C but not at 22.5 °C, OA decreased the growth of the copepod (*Acartia* sp.) nauplii population, implying a reduced top-down pressure on phytoplankton. In addition, inorganic macronutrient limitation alters the effect of OA on phytoplankton (Li et al. 2012a; Verspagen et al. 2014). Nitrate limitation and OA synergistically reduced the cell size and food value (N/C ratio) in a diatom (Li et al. 2012a). Limiting dissolved inorganic macronutrients reduce photosynthetic carbon fixation in phytoplankton under OA (Matthiessen et al. 2012).

Elevated levels of CO<sub>2</sub> and temperature synergistically decrease the maximal growth rates and shifted optimal growth temperatures of *E. huxleyi* towards lower levels over a broad temperature range from 15 to 27 °C (Listmann et al. 2016). Rising temperatures (from 15 to 25 °C) increased the maximal growth, POC and PIC production and shifted the temperature optimum for these physiological rates towards higher levels over a wide range of CO<sub>2</sub> concentrations (20–6000 µatm) in *E. huxleyi* and *G. oceanica* (Schlüter et al. 2014; Sett et al. 2014). However, results from other studies confirmed that effects of elevated CO<sub>2</sub> concentration on physiological rates were smaller at higher temperatures (De Bodt et al. 2010).

From these results, we derived a concept for the modulating effect of increasing CO<sub>2</sub> on the thermal reaction dependence (Fig. 5a) as well as the modulating effect of increasing temperature on the CO<sub>2</sub> response curve (Fig. 5b). At low limiting CO<sub>2</sub> levels, basically, low DIC concentrations control



**Fig. 5** Concept for the modulation effect of increasing CO<sub>2</sub> on the thermal reaction dependence (a) as well as the modulating effect of increasing temperature on the CO<sub>2</sub> response curve (b). Conceptual figure was based on the data of (Sett et al. 2014; Listmann et al. 2016)

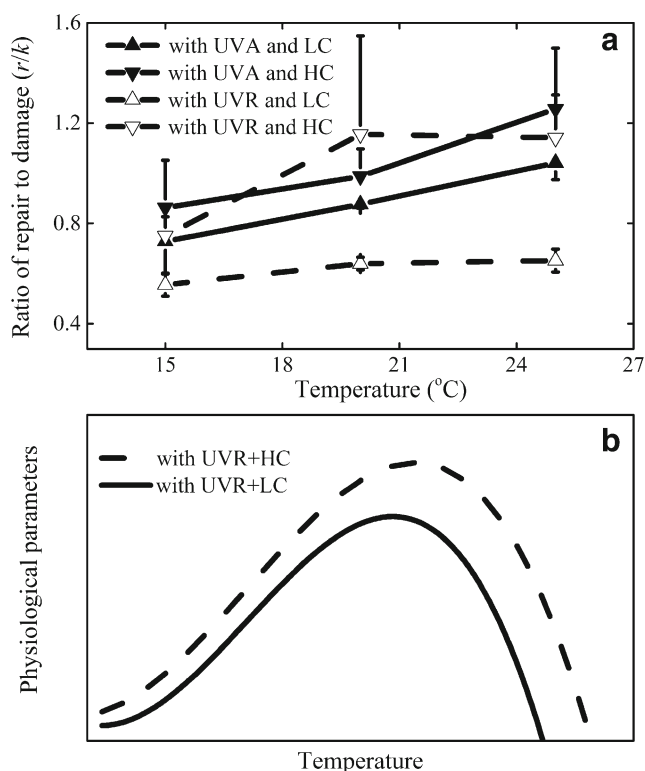
photosynthetic carbon fixation and phytoplankton growth rates, which increase very slowly with rising temperatures. Therefore, the temperature optimum for physiological reactions should not be clear at limiting low CO<sub>2</sub> levels. In contrast, at inhibiting high CO<sub>2</sub> concentration, the high H<sup>+</sup> concentration in the water impairs physiological reactions and even at low temperatures these can reach their maximum (Fig. 5a). At low limiting temperatures, physiological parameters are basically controlled by the temperature; increased CO<sub>2</sub> concentrations may have little effect on the physiological performances. Of course, there are exceptions: increased availability of CO<sub>2</sub> enhanced growth of a green tide alga to a larger extent at lower temperature (Xu et al. unpublished data). The synergistic negative effects of high temperature and elevated H<sup>+</sup> concentrations can be prevented by decreasing the CO<sub>2</sub> optima at inhibiting high temperatures (Fig. 5b).

Ocean warming can reduce the damaging effects of UVR on phytoplankton. The UV-inflicted damage is not only mitigated by increased temperatures but also by dissolved inorganic macronutrients (Doyle et al. 2005). At 6 °C and low dissolved inorganic macronutrient concentrations, UVR inhibited growth in the diatoms *Fragilaria crotonensis* and *Asterionella formosa*, the dinoflagellate *Gymnodinium* sp., and the chrysophyte *Dinobryon* sp., but at 14 °C the negative effect of UVR was mitigated. Phytoplankton assemblages showed less UV-induced inhibition of photosynthetic carbon fixation during summer than in winter periods (Wu et al.

2010). One explanation for this surprising result might be that elevated temperatures facilitated the repair of UV-induced thymine dimers and the synthesis of UV-absorbing pigments such as MAAs. Higher temperatures were reported to partially counteract UV inhibition on the photochemical efficiency ( $Y'$ ) in *Dunaliella salina*, *Isochrysis galbana*, *Chaetoceros gracilis*, and *Thalassiosira weissflogii*, but not in *P. micans* (Halac et al. 2010; Halac et al. 2014). Also, in *Gymnodinium chlorophorum*, the UV-inflicted inhibition of  $Y'$  decreased when the temperature was elevated from 15 °C to 20 °C, but it increased again when the temperature was raised to 25 °C, showing that the response followed an optimum curve (Häder et al. 2014). Garcia-Corral et al. (2015) also reported that a temperature increase by 3 °C worsened the negative effect of UV-B on net community production measured as oxygen exchange isolated from the Mediterranean Sea. However, it could not be determined whether productivity decreased with UV-B and temperature due to a decline in gross primary production or to an increase in community respiration. Photosynthetic carbon fixation and calcification rates

decreased when *E. huxleyi* was exposed to UVR but increased at elevated temperatures in the presence of high calcium concentrations (Xu et al. 2011); carbon fixation and calcification rates were higher at 25 °C than at 20 °C at all UV exposure conditions.

There are only a few short-term studies which investigated the combined effects of OA, increasing temperatures, and UVR on phytoplankton (Tong et al. 2017). In a diatom, growth at the elevated  $CO_2$  concentration (1000  $\mu\text{atm}$ ) increased its non-photochemical quenching (NPQ) and partially counteracted the harm to PSII caused by UV-A and UV-B. Such an effect was less pronounced under increased temperature levels. The ratio of repair to UV-B-induced damage decreased with increased NPQ, reflecting induction of NPQ when repair dropped below the damage (Li et al. 2012b). In addition, the ratio of repair to damage increased with increasing  $CO_2$  and temperatures (Fig. 6a). Consequently, these factors may interact synergistically and antagonistically to alter physiological responses to that of an individual stressor. This is dependent on the level of each factor and rising temperature or  $CO_2$  may mitigate the negative effect of UVR (Fig. 6b). Our knowledge on how multiple stressors, such as UVR, OA, and ocean warming, might interact under different climate scenario or in different regions is still limited due to a lack of understanding of the mechanisms of combined effects of  $CO_2$ , temperature, and UVR. Increased  $CO_2$  and temperature synergistically positively diminish the UV-induced inhibition and thereby augment the photosynthetic carbon fixation, e.g., in *Phaeodactylum tricornutum* (Li et al. 2012b); however, increasing  $CO_2$  concentrations or rising temperature may interact antagonistically or neutrally with UVR (Xu and Gao 2015).



**Fig. 6** Upper panel: OA and rising temperature increases the ratio of repair to damage induced by UV-A and UVR (UV-A + UV-B), suggesting OA and rising temperature mitigate the negative effect of UV-A and UV-B on physiological rates such as effective photochemical quantum yield ( $Y'$ ). Lower panel: conception for the effect of rising  $CO_2$  on the thermal reaction dependence under UVR. Rising  $CO_2$  mitigate the UVR-induced damage and may increase the optimum temperature and maximum physiological rates such as carbon fixation and  $Y'$  under UVR. LC indicates phytoplankton grew at 390  $\mu\text{atm}$   $CO_2$ , and HC indicates phytoplankton grew at 1000  $\mu\text{atm}$   $CO_2$  (Li et al. 2012b)

## Conclusion and perspectives

Individual effect of OA, OW, or UVR on physiological processes of phytoplankton has been studied in many species, but mainly under controlled laboratory conditions. Elevated temperatures have been reported to augment phytoplankton productivity because of elevated physiological reactions as well as increased enzymatic repair mechanisms. But increased temperatures may exceed the thermal window of some phytoplankton species and shift their habitats to higher latitudes. In some organisms, increasing  $CO_2$  concentration were reported to enhance photosynthesis, but others with efficient carbon concentration mechanisms may be hardly affected by increased  $CO_2$  concentration. Still higher  $CO_2$  concentrations result in OA interfering with the incrustation of carbonate and other physiological responses. Increased exposure to UV-B radiation has been reported to be deleterious to most aquatic primary producers but this can be mitigated by higher

temperatures (increased enzymatic repair) and sufficient dissolved inorganic macronutrient supply.

Studying the interactive effects of these stress factors has resulted in some unexpected and puzzling results. Further analysis has revealed that the reactions to the individual environmental factors follow specific optimum response curves such as for temperature and CO<sub>2</sub> concentration. In contrast, UVR results in damage which becomes worse with increasing irradiances.

Ocean warming and OA may result in synergistic, neutral, or antagonistic effects on physiological parameters. The result obtained at a higher temperature and low CO<sub>2</sub> might be equal to or higher than that under OA and lower temperature. In addition, the OA enhancement is usually higher at lower temperature. In some experiments, effects observed at a higher temperature and higher CO<sub>2</sub> could be lower than that under higher temperature and low CO<sub>2</sub>. In addition, inhibition or enhancement by OA on physiological parameters should be altered by changes in temperature. Therefore, it is necessary to compare the thermal windows under OA with non-OA conditions. This is also true for investigating the combined effects of temperature and UVR.

It is mandatory to understand the molecular and biochemical mechanisms of individual and combined effects of these quickly changing environmental stress factors in order to establish a reliable concept to understand responses of marine primary producers in different habitats. While it is technically challenging to investigate the responses of phytoplankton to natural stress factors such as OA, ocean warming, or UVR, investigating the effects of fluctuating multiple stress factors will require further studies. The outcome of these investigations is fundamental to comprehend the biogeochemical cycles in marine ecosystems and the carbon storage capacity of the oceans.

In both open oceans and coastal waters, OA and increasing temperatures are environmental stress factors of growing importance. Marine organisms and ecosystems are exposed to multifactorial stresses resulting from various effects of climate change; however, different regions are affected to different extents. For this reason, the effects of OA, OW, and exposure to higher UVR on phytoplankton productivity and community composition need to be studied under different natural and realistic scenarios. Clearly, responses of physiological rates of community composition to OA, OW, and UVR are different from that of single species. Thus, it would be preferential to study the response of phytoplankton community composition to multi-environmental factors such as OA, OW, UVR, dissolved inorganic macronutrients, Fe, rainfall, snow cover, alteration in upwelling patterns, and vitamin B<sub>12</sub>, but the vast regions of oceanic ecosystems and the experimental intricacies usually limit a thorough investigation under natural conditions with fluctuating or changing abiotic factors. At least these studies on phytoplankton should be carried out under

natural conditions rather than under controlled laboratory conditions. In addition, experimental designs to study the effects of multiple stressors are complicated and need to be well planned and performed. If a combination of several factors becomes logistically difficult to perform, sequential addition of stressors might be an option (Xing et al. 2015). In addition, experimental designs should reflect climate change effects on both bottom-up and top-down phytoplankton controls and consider how to evaluate phytoplankton adaptive strategies to climate change variables (Lohbeck et al. 2012; Schlüter et al. 2014; Gaitán-Espitia et al. 2017).

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## References

- Bach LT, Riebesell U, Gutowska MA, Federwisch L, Schulz KG (2015) A unifying concept of coccolithophore sensitivity to changing carbonate chemistry embedded in an ecological framework. *Prog Oceanogr* 135:125–138
- Bais A, McKenzie R, Bernhard G, Aucamp P, Ilyas M, Madronich S, Tourpali K (2015) Ozone depletion and climate change: impacts on UV radiation. *Photochem Photobiol Sci* 14:19–52
- Beardall J, Raven JA (2004) The potential effects of global climate change on microalgal photosynthesis, growth and ecology. *Phycologia* 43:26–40
- Beardall J, Stojkovic S, Gao K (2014) Interactive effects of nutrient supply and other environmental factors on the sensitivity of marine primary producers to ultraviolet radiation: implications for the impacts of global change. *Aquatic Biol* 22:5–23
- Behrenfeld M, O'Malley R, Siegel D, McClain C, Sarmiento J, Feldman G, Milligan A, Falkowski P, Letelier R, Boss E (2006) Climate-driven trends in contemporary ocean productivity. *Nature* 444:752–755
- Behrenfeld M, O'Malley R, Boss E, Westberry T, Graff J, Halsey KH, Milligan A, Siegel D, Brown M (2016) Revaluating ocean warming impacts on global phytoplankton. *Nat Clim Chang* 6:323–330
- Berthelot H, Moutin T, L'Helguen S, Leblanc K, Hélias S, Grosso O, Leblond N, Charrière B, Bonnet S (2015) Dinitrogen fixation and dissolved organic nitrogen fueled primary production and particulate export during the VAHINE mesocosm experiment (New Caledonia lagoon). *Biogeosciences* 12:4099–4112
- Böttjer D, Karl DM, Letelier RM, Viviani DA, Church MJ (2014) Experimental assessment of diazotroph responses to elevated seawater pCO<sub>2</sub> in the North Pacific Subtropical Gyre. *Glob Biogeochem Cycles* 28:601–616
- Boyce DG, Lewis MR, Worm B (2010) Global phytoplankton decline over the past century. *Nature* 466:591–596
- Boyd PW, Rynearson TA, Armstrong EA, Fu F, Hayashi K, Hu Z, Hutchins DA, Kudela RM, Litchman E, Mulholland MR, Passow U, Strzepek RF, Whittaker KS, Yu E, Thomas MK (2013) Marine phytoplankton temperature versus growth responses from polar to tropical waters—outcome of a scientific community-wide study. *PLoS One* 8:e63091
- Boyd PW (2011) Beyond ocean acidification. *Nat Geosci* 4:273–274

- Britton D, Cornwall CE, Reville AT, Hurd CL, Johnson CR (2016) Ocean acidification reverses the positive effects of seawater pH fluctuations on growth and photosynthesis of the habitat-forming kelp, *Ecklonia radiata*. *Scient Rep* 6:26036
- Buitenhuis ET, Pangerc T, Franklin DJ, Le Quéré C, Malin G (2008) Growth rates of six coccolithophorid strains as a function of temperature. *Limnol Oceanogr* 53:1181–1185
- Caldeira K, Wickett ME (2003) Oceanography: anthropogenic carbon and ocean pH. *Nature* 425:365–365
- Chavez FP, Messié M, Pennington JT (2011) Marine primary production in relation to climate variability and change. *Annu Rev Mar Sci* 3: 227–260
- Chen S, Gao K (2011) Solar ultraviolet radiation and CO<sub>2</sub>-induced ocean acidification interacts to influence the photosynthetic performance of the red tide alga *Phaeocystis globosa* (Prymnesiophyceae). *Hydrobiologia* 675:105–117
- Chen SW, Gao KS, Beardall J (2015) Viral attack exacerbates the susceptibility of a bloom-forming alga to ocean acidification. *Glob Chang Biol* 21:629–636
- Chivers WJ, Walne AW, Hays GC (2017) Mismatch between marine plankton range movements and the velocity of climate change. *Nat Commun* 8:14434
- Claquin P, Probert I, Lefebvre S, Veron B (2008) Effects of temperature on photosynthetic parameters and TEP production in eight species of marine microalgae. *Aquat Microb Ecol* 51:1–11
- Coello-Camba A, Agustí S, Holding J, Arrieta JM, Duarte CM (2014) Interactive effect of temperature and CO<sub>2</sub> increase in Arctic phytoplankton. *Front Mar Sci* 1:49
- Conte MH, Thompson A, Lesley D, Harris RP (1998) Genetic and physiological influences on the alkenone/alkenoate versus growth temperature relationship in *Emiliania huxleyi* and *Gephyrocapsa oceanica*. *Geochim Cosmochim Acta* 62:51–68
- Czerny J, Barcelos e Ramos J, Riebesell U (2009) Influence of elevated CO<sub>2</sub> concentrations on cell division and nitrogen fixation rates in the bloom-forming cyanobacterium *Nodularia spumigena*. *Biogeosciences* 6:1865–1875
- De Bodt C, Van Oostende N, Harlay J, Sabbe K, Chou L (2010) Individual and interacting effects of pCO<sub>2</sub> and temperature on *Emiliania huxleyi* calcification: study of the calcite production, the coccolith morphology and the coccosphere size. *Biogeosciences* 7: 1401–1412
- Domingues RB, Guerra CC, Galvão HM, Brotas V, Barbosa AB (2017) Short-term interactive effects of ultraviolet radiation, carbon dioxide and nutrient enrichment on phytoplankton in a shallow coastal lagoon. *Aquatic Ecol* 51:91–105
- Doyle SA, Saros JE, Williamson CE (2005) Interactive effects of temperature and nutrient limitation on the response of alpine phytoplankton growth to ultraviolet radiation. *Limnol Oceanogr* 50:1362–1367
- Edward M, Richardson AJ (2004) Impact of climate change on marine pelagic phenology and trophic mismatch. *Nature* 430:881–884
- Ehlert D, Zickfeld K, Eby M, Gillett N (2017) The sensitivity of the proportionality between temperature change and cumulative CO<sub>2</sub> emissions to ocean mixing. *J Clim* 30. doi: <https://doi.org/10.1175/JCLI-D-16-0247.s1>
- Eichner M, Rost B, Kranz SA (2014) Diversity of ocean acidification effects on marine N<sub>2</sub> fixers. *J Exp Mar Biol Ecol* 457:199–207
- Engel A, Piontek J, Grossart H-P, Riebesell U, Schulz KG, Sperling M (2014) Impact of CO<sub>2</sub> enrichment on organic matter dynamics during nutrient induced coastal phytoplankton blooms. *J Plankton Res* 36:641–657
- Field CB, Behrenfeld MJ, Randerson JT, Falkowski P (1998) Primary production of the biosphere: integrating terrestrial and oceanic components. *Science* 281:237–240
- Fu FX, Tatters AO, Hutchins DA (2012) Global change and the future of harmful algal blooms in the ocean. *Mar Ecol Prog Ser* 470:207–233
- Gaitán-Espitia JD, Marshall D, Dupont S, Bacigalupe LD, Bodrossy L, Hobday AJ (2017) Geographical gradients in selection can reveal genetic constraints for evolutionary responses to ocean acidification. *Biol Lett* 13:20160784
- Gao K, Campbell D (2014) Photophysiological responses of marine diatoms to elevated CO<sub>2</sub> and decreased pH: a review. *Funct Plant Biol* 41:449–459
- Gao K, Helbling EW, Häder D-P, Hutchins DA (2012a) Responses of marine primary producers to interactions between ocean acidification, solar radiation, and warming. *Mar Ecol Prog Ser* 470:167–189
- Gao K, Ruan Z, Villafañe VE, Gattuso JP, Helbling EW (2009) Ocean acidification exacerbates the effect of UV radiation on the calcifying phytoplankter *Emiliania huxleyi*. *Limnol Oceanogr* 54:1855–1862
- Gao K, Wu Y, Li G, Wu H, Villafañe VE, Helbling EW (2007) Solar UV radiation drives CO<sub>2</sub> fixation in marine phytoplankton: a double-edged sword. *Plant Physiol* 144:54–59
- Gao K, Zheng Y (2010) Combined effects of ocean acidification and solar UV radiation on photosynthesis, growth, pigmentation and calcification of the coralline alga *Corallina sessilis* (Rhodophyta). *Glob Chang Biol* 16:2388–2398
- Gao KS, JT X, Gao G, Li YH, Hutchins DA, Huang BQ, Wang L, Zheng Y, Jin P, Cai XN, Häder DP, Li W, Xu K, Liu NN, Riebesell U (2012b) Rising CO<sub>2</sub> and increased light exposure synergistically reduce marine primary productivity. *Nat Clim Chang* 2:519–523
- García-Corral LS, Martínez-Ayala J, Duarte CM, Agustí S (2015) Experimental assessment of cumulative temperature and UV-B radiation effects on Mediterranean plankton metabolism. *Front Mar Sci* 2:48
- Gargett A, Marra J (2002) Effects of upper ocean physical processes (turbulence, advection and air-sea interaction) on oceanic primary production. *The Sea* 12:19–49
- Gattuso J-P, Magnan A, Billé R, Cheung W, Howes E, Joos F, Allemand D, Bopp L, Cooley S, Eakin C (2015) Contrasting futures for ocean and society from different anthropogenic CO<sub>2</sub> emissions scenarios. *Science* 349(6243):aac4722
- Geider RJ, MacIntyre HL, Kana TM (1997) A dynamic model of phytoplankton growth and acclimation: responses of the balanced growth rate and chlorophyll *a*:carbon ratio to light, nutrient-limitation and temperature. *Mar Ecol Prog Ser* 148:187–200
- Gradoville MR, White AE, Böttjer D, Church MJ, Letelier RM (2014) Diversity trumps acidification: lack of evidence for carbon dioxide enhancement of *Trichodesmium* community nitrogen or carbon fixation at Station ALOHA. *Limnol Oceanogr* 59:645–659
- Grear JS, Ryneanson TA, Montalbano AL, Govenar B, Menden-Deuer S (2017) pCO<sub>2</sub> effects on species composition and growth of an estuarine phytoplankton community. *Estuar Coast Shelf Sci* 190:40–49
- Groetsch PM, Simis SG, Eleveld MA, Peters SW (2016) Spring blooms in the Baltic Sea have weakened but lengthened from 2000 to 2014. *Biogeosciences* 13(17):4959
- Guan W, Li P (2017) Dependency of UVR-induced photoinhibition on atomic ratio of N to P in the dinoflagellate *Karenia mikimotoi*. *Mar Biol* 164(2):31
- Häder D-P, Gao K (2015) Interactions of anthropogenic stress factors on marine phytoplankton. *Front Env Sci* 3:14
- Häder D-P, Richter P, Villafañe VE, Helbling EW (2014) Influence of light history on the photosynthetic and motility responses of *Gymnodinium chlorophorum* exposed to UVR and different temperatures. *J Photochem Photobiol B* 138:273–281
- Häder D-P, Williamson CE, Wangberg S-A, Rautio M, Rose KC, Gao K, Helbling EW, Sinha RP, Worrest R (2015) Effects of UV radiation on aquatic ecosystems and interactions with other environmental factors. *Photochem Photobiol Sci* 14:108–126. <https://doi.org/10.1039/C4PP90035A>
- Halac S, Villafañe V, Gonçalves R, Helbling E (2014) Photochemical responses of three marine phytoplankton species exposed to

- ultraviolet radiation and increased temperature: role of photoprotective mechanisms. *J Photochem Photobiol B* 141:217–227
- Halac SR, Guendulain-García SD, Villafañe VE, Helbling EW, Banaszak AT (2013) Responses of tropical plankton communities from the Mexican Caribbean to solar ultraviolet radiation exposure and increased temperature. *J Exp Mar Biol Ecol* 445:99–107
- Halac SR, Villafañe VE, Helbling EW (2010) Temperature benefits the photosynthetic performance of the diatoms *Chaetoceros gracilis* and *Thalassiosira weissflogii* when exposed to UVR. *J Photochem Photobiol B* 101:196–205
- Hansell DA, Carlson CA (2014) Biogeochemistry of marine dissolved organic matter. Academic Press
- Hansen J, Sato M, Ruedy R, Lo K, Lea DW, Medina-Elizade M (2006) Global temperature change. *Proc Nat Acad Sci* 103:14288–14293
- Hattenrath-Lehmann TK, Smith JL, Wallace RB, Merlo LR, Koch F, Mittelsdorf H, Goleski JA, Anderson DM, Gobler CJ (2015) The effects of elevated CO<sub>2</sub> on the growth and toxicity of field populations and cultures of the saxitoxin-producing dinoflagellate, *Alexandrium fundyense*. *Limnol Oceanogr* 60:198–214
- Henson SA, Beaulieu C, Lampitt R (2016) Observing climate change trends in ocean biogeochemistry: when and where. *Glob Chang Biol* 22:1561–1571
- Hoffmann L, Hoppe CM, Müller R, Dutton GS, Gille JC, Griessbach S, Jones A, Meyer CI, Spang R, Volk CM, Walker KA (2014) Stratospheric lifetime ratio of CFC-11 and CFC-12 from satellite and model climatologies. *Atmos Chem Phys* 14:12479–12497
- Holding JM, Duarte CM, Sanz-Martín M, Mesa E, Arrieta JM, Chierici M, Hendriks I, Garcia-Corral L, Regaudie-de-Gioux A, Delgado A (2015) Temperature dependence of CO<sub>2</sub>-enhanced primary production in the European Arctic Ocean. *Nat Clim Chang* 5:1079–1082
- Hönisch B, Ridgwell A, Schmidt DN, Thomas E, Gibbs SJ, Sluijs A, Zeebe R, Kump L, Martindale RC, Greene SE (2012) The geological record of ocean acidification. *Science* 335:1058–1063
- Honjo S, Eglinton TI, Taylor CD, Ulmer KM, Sievert SM, Bracher A, German CR, Edgcomb V, Francois R, Inglesias-Rodriguez MD (2014) Understanding the role of the biological pump in the global carbon cycle: an imperative for ocean science. *Oceanography* 27:10–16
- Huey RB, Stevenson R (1979) Integrating thermal physiology and ecology of ectotherms: a discussion of approaches. *Am Zool* 19:357–366
- Hutchins DA, F-X F, Webb EA, Walworth N, Tagliabue A (2013) Taxon-specific response of marine nitrogen fixers to elevated carbon dioxide concentrations. *Nat Geosci* 6:790–795
- Hutchins DA, Walworth NG, Webb EA, Saito MA, Moran D, McIlvin MR, Gale J, F-X F (2015) Irreversibly increased nitrogen fixation in *Trichodesmium* experimentally adapted to elevated carbon dioxide. *Nat Commun* 6
- Hyun B, Choi K-H, Jang P-G, Jang M-C, Lee W-J, Moon C-H, Shin K (2014) Effects of increased CO<sub>2</sub> and temperature on the growth of four diatom species (*Chaetoceros debilis*, *Chaetoceros didymus*, *Skeletonema costatum* and *Thalassiosira nordenskiöldii*) in laboratory experiments. *J Env Sci Internat* 23:1003–1012
- IPCC (2014) Climate change 2014: impacts, adaptation, and vulnerability. Part B: Regional Aspects Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change vol 2014
- Jin P, Ding J, Xing T, Riebesell U, Gao K (2017) High levels of solar radiation offset impacts of ocean acidification on *Emiliania huxleyi*, with special reference to calcifying and non-calcifying strains. *Mar Ecol Prog Ser* 568:47–58
- Jin P, Gao K, Villafañe V, Campbell D, Helbling W (2013) Ocean acidification alters the photosynthetic responses of a coccolithophorid to fluctuating ultraviolet and visible radiation. *Plant Physiol* 162:2084–2094
- Jin P, Wang T, Liu N, Dupont S, Beardall J, Boyd PW, Riebesell U, Gao K (2015) Ocean acidification increases the accumulation of toxic phenolic compounds across trophic levels. *Nat Commun* 6:8714
- Kaeriyama H, Katsuki E, Otsubo M, Yamada M, Ichimi K, Tada K, Harrison PJ (2011) Effects of temperature and irradiance on growth of strains belonging to seven *Skeletonema* species isolated from Dokai Bay, southern Japan. *Eur J Phycol* 46:113–124
- Kim J-H (2006) The effect of seawater CO<sub>2</sub> concentration on growth of a natural phytoplankton assemblage in a controlled mesocosm experiment. *Limnol Oceanogr* 51:1629–1636
- Kleypas JA, Feely RA, Fabry VJ, Langdon C, Sabine CL, Robbins LL (2006) Impacts of ocean acidification on coral reefs and other marine calcifiers: a guide for future research. Workshop held 18–20 April 2005, St. Petersburg, FL, sponsored by NSF, NOAA, and the U.S. Geological Survey
- Kremp A, Godhe A, Egardt J, Dupont S, Suikkanen S, Casabianca S, Penna A (2012) Intraspecific variability in the response of bloom-forming marine microalgae to changed climate conditions. *Ecol Evol* 2:1195–1207
- Lammers JM, van Soelen EE, Donders TH, Wagner-Cremer F, Sinnighe Damsté JS, Reichart GJ (2013) Natural environmental changes versus human impact in a Florida Estuary (Rookery Bay, USA). *Estuar Coasts* 36:149–157
- Landschützer P, Gruber N, Bakker D, Schuster U (2014) Recent variability of the global ocean carbon sink. *Glob Biogeochem Cycles* 28:927–949
- Larsen J, Larsen A, Thyrrhaug R, Bratbak G, Sandaa R-A (2008) Response of marine viral populations to a nutrient induced phytoplankton bloom at different pCO<sub>2</sub> levels. *Biogeosciences* 5:523–533
- Leung PT, Yi AX, Ip JC, Mak SS, Leung KM (2017) Photosynthetic and transcriptional responses of the marine diatom *Thalassiosira pseudonana* to the combined effect of temperature stress and copper exposure. *Mar Poll Bull*. <https://doi.org/10.1016/j.marpolbul.2017.03.038>
- Li G, Gao K (2013) Cell size-dependent effects of solar UV radiation on primary production in coastal waters of the South China Sea. *Estuar Coasts* 36:728–736
- Li G, Gao K, Gao G (2011) Differential impacts of solar UV radiation on photosynthetic carbon fixation from the coastal to offshore surface waters in the South China Sea. *Photochem Photobiol* 87:329–334
- Li G, Wu Y, Gao K (2009) Effects of Typhoon Kaemi on coastal phytoplankton assemblages in the South China Sea, with special reference to the effects of solar UV radiation. *J Geophys Res Biogeosci* 114(G4)
- Li W, Gao K, Beardall J (2012a) Interactive effects of ocean acidification and nitrogen-limitation on the diatom *Phaeodactylum tricornutum*. *PLoS One* 7(12):e51590
- Li W, Gao KS (2012) A marine secondary producer respire and feeds more in a high CO<sub>2</sub> ocean. *Mar Poll Bull* 64:699–703
- Li W, Yang Y, Li Z, Xu J, Gao K (2016) Effects of seawater acidification on the growth rates of the diatom *Thalassiosira (Conticribra) weissflogii* under different nutrient, light, and UV radiation regimes. *J Appl Phycol* 29:133–142
- Li Y, Gao K, Villafañe V, Helbling E (2012b) Ocean acidification mediates photosynthetic response to UV radiation and temperature increase in the diatom *Phaeodactylum tricornutum*. *Biogeosciences* 9:3931–3942
- Listmann L, LeRoch M, Schlüter L, Thomas MK, Reusch TB (2016) Swift thermal reaction norm evolution in a key marine phytoplankton species. *Evol Appl* 9:1156–1164
- Liu N, Beardall J, Gao K (2017) Elevated CO<sub>2</sub> and associated seawater chemistry do not benefit a model diatom grown with increased availability of light. *Aquat Microb Ecol* 79:137–147
- Lohbeck K, Riebesell U, Reusch T (2012) Adaptive evolution of a key phytoplankton species to ocean acidification. *Nat Geosci* 5:346–351

- Mackey KR, Morris JJ, Morel FM, Kranz SA (2015) Response of photosynthesis to ocean acidification. *Oceanography* 28:74–91
- Manney GL, Santee ML, Rex M, Livesey NJ, Pitts MC, Veefkind P, Nash ER, Wohltmann I, Lehmann R, Froidevaux L, Poole LR, Schoeberl MR, Haffner DP, Davies J, Dorokhov V, Gernandt H, Johnson B, Kivi R, Kyrö E, Larsen N, Levelt PF, Makshtas A, McElroy CT, Nakajima H, Parrondo MC, Tarasick DW, von der Gathen P, Walker KA, Zinoviev NS (2011) Unprecedented Arctic ozone loss in 2011. *Nature*:469–475
- Marchese C, Albouy C, Tremblay J-É, Dumont D, D’Ortenzio F, Vissault S, Bélanger S (2017) Changes in phytoplankton bloom phenology over the North Water (NOW) polynya: a response to changing environmental conditions. *Polar Biol* 40:1721–1737
- Matthiessen B, Eggers SL, Krug S (2012) High nitrate to phosphorus regime attenuates negative effects of rising pCO<sub>2</sub> on total population carbon accumulation. *Biogeosciences* 9:1195–1203
- McKenzie RL, Aucamp PJ, Bais AF, Björn LO, Ilyas M, Madronich S (2011) Ozone depletion and climate change: impacts on UV radiation. *Photochem Photobiol Sci* 10:182–198
- Meador JA, Baldwin AJ, Catala P, Jeffrey WH, Joux F, Moss JA, Pakulski JD, Stevens R, Mitchell DL (2009) Sunlight-induced DNA damage in marine micro-organisms collected along a latitudinal gradient from 70 °N to 68 °S. *Photochem Photobiol* 85:412–421
- Michaels AF, Karl DM, Capone DG (2001) Element stoichiometry, new production and nitrogen fixation. *Oceanography* 14:68–77
- Millero FJ (2007) The marine inorganic carbon cycle. *Chem Rev* 107:308–341
- Milner S, Langer G, Grelaud M, Ziveri P (2016) Ocean warming modulates the effects of acidification on *Emiliania huxleyi* calcification and sinking. *Limnol Oceanogr* 61:1322–1336
- Miyairi S (1995) CO<sub>2</sub> assimilation in a thermophilic cyanobacterium. *Energy Convers Manag* 36:763–766
- Moisan TA, Goes J, Neale PJ (2009) Mycosporine-like amino acids in phytoplankton: biochemistry, physiology and optics. In: Kersey WT, Munger SP (eds) *Marine phytoplankton*. Nova Science Publishers, New York, pp 119–143
- Montagnes DJ, Franklin M (2001) Effect of temperature on diatom volume, growth rate, and carbon and nitrogen content: reconsidering some paradigms. *Limnol Oceanogr* 46:2008–2018
- Monteiro FM, Bach LT, Brownlee C, Bown P, Rickaby RE, Poulton AJ, Tyrrell T, Beaufort L, Dutkiewicz S, Gibbs S (2016) Why marine phytoplankton calcify. *Sci Adv* 2(7):e1501822
- Neale PJ, Helbling EW, Zagarese HE (2003) Modulation of UVR exposure and effects by vertical mixing and advection. In: Helbling EW, Zagarese H (eds) *UV Effects in aquatic organisms and ecosystems*, vol 1. The royal society of chemistry, London pp 107–134
- Newman PA, McKenzie RL (2011) UV impacts avoided by the Montreal Protocol. *Photochem Photobiol Sci* 10:1152–1160.
- Nick FM, Vieli A, Andersen ML, Joughin I, Payne A, Edwards TL, Pattyn F, van de Wal RS (2013) Future sea-level rise from Greenland’s main outlet glaciers in a warming climate. *Nature* 497:235–238
- Orr JC, Fabry VJ, Aumont O, Bopp L, Doney SC, Feely RA, Gnanadesikan A, Gruber N, Ishida A, Joos F, Key RM, Lindsay K, Maier-Reimer E, Matar R, Monfray P, Mouchet A, Najjar RG, Plattner GK, Rodgers KB, Sabine CL, Sarmiento JL, Schlitzer R, Slater RD, Totterdell IJ, Weirig MF, Yamanaka Y, Yool A (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* 437:681–686
- Paul C, Sommer U, Garzke J, Moustaka-Gouni M, Paul A, Matthiessen B (2016) Effects of increased CO<sub>2</sub> concentration on nutrient limited coastal summer plankton depend on temperature. *Limnol Oceanogr* 61:853–868
- Piazena H, Perez-Rodriguez E, Häder D-P, Lopez-Figueroa F (2002) Penetration of solar radiation into the water column of the central subtropical Atlantic Ocean—optical properties and possible biological consequences. *Deep-Sea Res II* 49:3513–3528
- Rastogi R, Singh S, Incharoensakdi A, Häder D-P, Sinha R (2014) Ultraviolet radiation-induced generation of reactive oxygen species, DNA damage and induction of UV-absorbing compounds in the cyanobacterium *Rivularia* sp. HKAR-4. *S Afr J Bot* 90:163–169
- Raven J, Caldeira K, Elderfield H, Hoegh-Guldberg O, Liss P, Riebesell U, Shepherd J, Turley C, Watson A (2005) *Ocean acidification due to increasing atmospheric carbon dioxide*. Policy Document 12/05. The Royal Society, London, p 57
- Raymont JE (2014) *Plankton & productivity in the oceans: Volume 1: Phytoplankton*. Elsevier
- Richa, Sinha RP, Häder D-P (2016) Effects of global change, including UV and UV screening compounds. In: Borowitzka MA, Beardall J, Raven J (eds) *The physiology of microalgae*. Springer, Cham, pp 373–409
- Riebesell U, Gattuso J-P (2015) Lessons learned from ocean acidification research. *Nat Clim Chang* 5(1):12–14
- Riebesell U, Schulz KG, Bellerby RGJ, Botros M, Fritsche P, Meyerhöfer M, Neill C, Nondal G, Oschlies A, Wohlers J, Zöllner E (2007) Enhanced biological carbon consumption in a high CO<sub>2</sub> ocean. *Nature* 450:545–548
- Riebesell U, Tortell PD (2011) Effects of ocean acidification on pelagic organisms and ecosystems. In: Gattuso JP, Hansson L (eds) *Ocean acidification*. Oxford University Press, Oxford, pp 99–116
- Rind D, Suozzo R, Balachandran N, Prather M (1990) Climate change and the middle atmosphere. Part I: the doubled CO<sub>2</sub> climate. *J Atmos Sci* 47:475–494
- Rosas-Navarro A, Langer G, Ziveri P (2016) Temperature affects the morphology and calcification of *Emiliania huxleyi* strains. *Biogeosciences* 13:2913–2926
- Rose JM, Feng Y, DiTullio GR, Dunbar RB, Hare CE, Lee PA, Lohan M, Long M, Smith WO Jr, Sohst B, Tozzi S, Zhang Y, Hutchins DA (2009) Synergistic effects of iron and temperature on Antarctic phytoplankton and microzooplankton assemblages. *Biogeosciences* 6:3131–3147
- Sabine CL, Feely RA, Gruber N, Key RM, Lee K, Bullister JL, Wanninkhof R, Won CS, Wallace DWR, Tilbrook B, Millero FJ, Peng T-H, Kozyr A, Ono T, Rios AF (2004) The oceanic sink for anthropogenic CO<sub>2</sub>. *Science* 305:367–371
- Schädel C, Bader MK-F, Schuur EA, Biasi C, Bracho R, Čapek P, De Baets S, Diáková K, Ernakovich J, Estop-Aragones C (2016) Potential carbon emissions dominated by carbon dioxide from thawed permafrost soils. *Nat Clim Chang* 6:950–953
- Schlüter L, Lohbeck KT, Gutowska MA, Gröger JP, Riebesell U, Reusch TB (2014) Adaptation of a globally important coccolithophore to ocean warming and acidification. *Nat Clim Chang* 4:1024–1030
- Sett S, Bach LT, Schulz KG, Koch-Klavnsen S, Lebrato M, Riebesell U (2014) Temperature modulates coccolithophorid sensitivity of growth, photosynthesis and calcification to increasing seawater pCO<sub>2</sub>. *PLoS One* 9(2):e88308
- Shi D, Kranz SA, Kim J-M, Morel FM (2012) Ocean acidification slows nitrogen fixation and growth in the dominant diazotroph *Trichodesmium* under low-iron conditions. *Proc Nat Acad Sci* 109:E3094–E3100
- Siegel DA, Brehenfeld MJ, Maritorea S, McClain CR, Antoine D, Bailey SW, Bontempi PS, Boss ES, Dierssen HM, Doney SC (2013) Regional to global assessments of phytoplankton dynamics from the SeaWiFS mission. *Remote Sens Environ* 135:77–91
- Solomon S, Ivy DJ, Kinnison D, Mills MJ, Neely RR, Schmidt A (2016) Emergence of healing in the Antarctic ozone layer. *Science* 353:269–274
- Stahelin J, Harris NRP, Appenzeller C, Eberhard J (2001) Ozone trends: a review. *Rev Geophys* 39:231–290
- Steinacher M, Joos F, Froelicher TL, Bopp L, Cadule P, Cocco V, Doney SC, Gehlen M, Lindsay K, Moore JK, Schneider B, Segsneider J



- (2010) Projected 21st century decrease in marine productivity: a multi-model analysis. *Biogeosciences* 7:979–1005
- Steinberg DK, Nelson NB, Craig AC, Prusak A (2004) Production of chromophoric dissolved organic matter (CDOM) in the open ocean by zooplankton and the colonial cyanobacterium *Trichodesmium* spp. *Mar Ecol Prog Ser* 267:45–56
- Stolarski RS (1988) The Antarctic ozone hole. *Sci Am* 258:20–26
- Sun J, Hutchins DA, Feng Y, Seubert EL, Caron DA, F-X F (2011) Effects of changing pCO<sub>2</sub> and phosphate availability on domoic acid production and physiology of the marine harmful bloom diatom *Pseudo-nitzschia multiseriata*. *Limnol Oceanogr* 56:829–840
- Suzuki Y, Takahashi M (1995) Growth responses of several diatom species isolated from various environments to temperature. *J Phycol* 31: 880–888
- Thomas MK, Kremer CT, Klausmeier CA, Litchman E (2012) A global pattern of thermal adaptation in marine phytoplankton. *Science* 338: 1085–1088
- Tilstone G, Šedivá B, Tarran G, Kaňa R, Prášil O (2016) Effect of CO<sub>2</sub> enrichment on phytoplankton photosynthesis in the North Atlantic sub-tropical gyre. *Progr Oceanogr*. <https://doi.org/10.1016/j.pocean.2016.12.005>
- Tong S, Hutchins D, Gao K (2017) Physiological and biochemical responses of *Emiliania huxleyi* to ocean acidification and warming are modulated by UV radiation. *Biogeosci Discuss*. <https://doi.org/10.5194/bg-2017-269>
- Tortell PD, DiTullio GR, Sigman DM, Morel FM (2002) CO<sub>2</sub> effects on taxonomic composition and nutrient utilization in an equatorial Pacific phytoplankton assemblage. *Mar Ecol Prog Ser* 236:37–43
- Tortell PD, Rau GH, Morel FM (2000) Inorganic carbon acquisition in coastal Pacific phytoplankton communities. *Limnol Oceanogr* 45: 1485–1500
- United Nations Environment Programme Environmental Effects Assessment Panel (2017) Environmental effects of ozone depletion and its interactions with climate change: progress report, 2016. *Photochem Photobiol Sci* 16:107–145
- Van de Waal DB, Verspagen JMH, Finke JF, Vournazou V, Immers AK, Kardinaal WEA, Tonk L, Becker S, Van Donk E, Visser PM, Huisman J (2011) Reversal in competitive dominance of a toxic versus non-toxic cyanobacterium in response to rising CO<sub>2</sub>. *ISME J* 5:1438–1450
- Verspagen JM, Van de Waal DB, Finke JF, Visser PM, Huisman J (2014) Contrasting effects of rising CO<sub>2</sub> on primary production and ecological stoichiometry at different nutrient levels. *Ecol Lett* 17:951–960
- Villafañe VE, Gao K, Li P, Helbling EW (2007) Vertical mixing within the epilimnion modulates UVR-induced photoinhibition in tropical freshwater phytoplankton from southern China. *Freshw Biol* 52: 1260–1270
- Villar-Argaiz M, Balseiro E, Modenutti B, Souza M, Bullejos F, Medina-Sánchez J, Carrillo P (2017) Resource versus consumer regulation of phytoplankton: testing the role of UVR in a Southern and Northern hemisphere lake. *Hydrobiologia* <https://doi.org/10.1007/s10750-017-3251-y>
- Wallington TJ, Schneider WF, Worsnop DR, Nielsen OJ, Sehested J, Debruyn WJ, Shorter JA (1994) The environmental impact of CFC replacements HFCs and HCFCs. *Envi Sci Technol* 28:320A–326A
- Wang G, Xie S-P, Huang RX, Chen C (2015) Robust warming pattern of global subtropical oceans and its mechanism. *J Clim* 28:8574–8584
- Wannicke N, Endres S, Engel A, Grossart H-P, Nausch M, Unger J, Voss M (2012) Response of *Nodularia spumigena* to pCO<sub>2</sub>—part 1: growth, production and nitrogen cycling. *Biogeosciences* 9:2973–2988
- van Wells ML, Trainer VL, Smayda TJ, Karlson BS, Trick CG, Kudela RM, Ishikawa A, Bernard S, Wulff A, Anderson DM (2015) Harmful algal blooms and climate change: learning from the past and present to forecast the future. *Harmful Algae* 49:68–93
- Wu X, Gao G, Giordano M, Gao K (2012) Growth and photosynthesis of a diatom grown under elevated CO<sub>2</sub> in the presence of solar UV radiation. *Fund Appl Limnol* 180:279–290
- Wu Y, Gao K, Riebesell U (2010) CO<sub>2</sub>-induced seawater acidification affects physiological performance of the marine diatom *Phaeodactylum tricoratum*. *Biogeosciences* 7:2915–2923
- Xing T, Gao K, Beardall J (2015) Response of growth and photosynthesis of *Emiliania huxleyi* to visible and UV irradiances under different light regimes. *Photochem Photobiol* 91:343–349
- Xu J, Gao K, Li Y, Hutchins DA (2014) Multiple future ocean changes interactively alter physiological and biochemical processes of diatoms. *Mar Ecol Prog Ser* 515:73–81
- Xu K, Gao K (2015) Solar UV irradiances modulate effects of ocean acidification on the Coccolithophorid *Emiliania huxleyi*. *Photochem Photobiol* 91:92–101
- Xu K, Gao K, Villafañe V, Helbling E (2011) Photosynthetic responses of *Emiliania huxleyi* to UV radiation and elevated temperature: roles of calcified coccoliths. *Biogeosciences* 8:1441–1452
- Zeebe RE (2012) History of seawater carbonate chemistry, atmospheric CO<sub>2</sub>, and ocean acidification. *Annu Rev Earth Planet Sci* 40:141–165
- Zeebe RE, Wolf-Gladrow DA (2001) CO<sub>2</sub> in seawater: equilibrium, kinetics, isotopes. Elsevier, Amsterdam
- Zhang Y, Bach LT, Schulz KG, Riebesell U (2015) The modulating effect of light intensity on the response of the coccolithophore *Gephyrocapsa oceanica* to ocean acidification. *Limnol Oceanogr* 60:2145–2157
- Zhang Y, Jiang HB, Qiu BS (2013) Effects of UVB radiation on competition between the bloom-forming cyanobacterium *Microcystis aeruginosa* and the Chlorophyceae *Chlamydomonas microspora*. *J Phycol* 49:318–328
- Zhang Y, Klapper R, Lohbeck KT, Bach LT, Schulz KG, Reusch TB, Riebesell U (2014) Between-and within-population variations in thermal reaction norms of the coccolithophore *Emiliania huxleyi*. *Limnol Oceanogr* 59:1570–1580