Reviews and Syntheses: Ocean acidification and its potential impacts on marine ecosystems

By

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Abstract

Ocean acidification, a complex phenomenon that lowers seawater pH, is the net outcome of several contributions. They include the dissolution of increasing atmospheric CO_2 that adds up with dissolved inorganic carbon (dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}) generated upon mineralization of primary producers (PP) and dissolved organic matter (DOM). The aquatic processes leading to inorganic carbon are substantially affected by increased DOM and nutrients *via* terrestrial runoff, acidic rainfall, increased PP and algal blooms, nitrification, denitrification, sulfate reduction, global warming (GW), and by atmospheric CO_2 itself through enhanced photosynthesis. They are consecutively associated with enhanced ocean acidification, hypoxia in acidified deeper seawater, pathogens, algal toxins, oxidative stress by reactive oxygen species, and thermal stress caused by longer stratification periods as an effect of GW. We discuss the mechanistic insights into the aforementioned processes and pH changes, with particular focus on processes taking place with different time scales (including the diurnal one) in surface and subsurface seawater. This review also discusses these collective influences to assess their potential detrimental effects to marine organisms, and of ecosystem processes and services. Our review of the effects operating in synergy with ocean acidification will provide a broad insight into the potential impact of acidification itself on biological processes. The foreseen danger to marine organisms by acidification is in fact expected to be amplified by several concurrent and interacting phenomena.

Keywords: Acidification; CO_2; organic matter; biological processes; global warming; photosynthesis, impacts on marine organisms.

1 Introduction

Ocean acidification is typically defined as a process of increasing seawater acidity or lowering seawater pH, as a consequence of the dissolution of elevated atmospheric CO_2. Carbon dioxide from the atmosphere (Orr et al., 2005; Feely et al., 2008) adds to the dissolved inorganic carbon (DIC: dissolved CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}) originated from the degradation of dissolved organic matter (DOM) (Mostofa et al., 2013a), primary producers (PP) (Cai et al., 2011; Mostofa et al., 2013a), CO_2 seeps from sub-seabed storage (Taylor et al., 2014) and volcanic vents (Lidbury et al., 2012; Hall-Spencer et al., 2008) in shallow submarine zones, anaerobic oxidation of methane (Haroon et al., 2013) and sulphide oxidation coupled to carbonate dissolution (Torres et al., 2014) in seawater. The sources of elevated atmospheric CO_2 include first of all anthropogenic activities such as fossil fuels combustion (such as coal, petroleum and natural gas (Le Quéré et al., 2009), enhanced land-use practices (Le Quéré et al., 2009), as well as deforestation (van der Werf et al., 2009; Lapola et al., 2014). Additionally, there could be significant contributions from natural sources such as plant litter decomposition (King et al., 2012), volcanic eruptions (Hall-Spencer et al., 2008), emission of CO_2 from freshwater including the Amazon River basin (Sobek et al., 2005; Abril et al., 2014) and enhanced respiration of soil organic matter (OM) under global warming (GW) conditions (Knorr et al., 2005).

The emissions of CO_2 by fossil fuels combustion have increased by 29% in 2000-2008 (Le Quéré et al., 2009) and, as far as natural-water sources are concerned, the contribution from European estuaries is for instance equivalent to approximately 5 to 10% of the anthropogenic CO_2 emissions in Western Europe (Frankignoulle et al., 1998).

Recent studies demonstrate that ocean acidification under elevated CO_2 and temperature levels could increase primary productivity of specific species (Holding et al., 2015; Coello-Camba et al. 2014; Li et al., 2012). Additionally, such specific species-based primary productivity is also found to increase either by increasing seawater CO_2 level (Kim et al., 2006; Olischläger et al., 2013) or elevated temperature alone because of the effects of global warming (Yvon-Durocher et al., 2015; Lewandowska et al., 2012). The primary production in the oceans contributes approximately 48.5 petagrams (1 Pg = 10^{15} g) of C yr^{-1} (46.2% of the total), as estimated using the integrated CASA-VGPM biosphere model (Field et al., 1998). As a consequence, approximately one-third to 50% of the atmospheric CO_2 is fixed annually worldwide by marine phytoplankton (Sabine et al., 2004; Toseland et al., 2013). However, one should also consider that the photoinduced and biological mineralization of organic matter (OM), including DOM and dead organisms, is an important source of DIC in seawater and liberates again an important fraction of the CO_2 fixed by photosynthesis (Bates and Mathis, 2009; Mostofa et al., 2013a).

Ocean acidification is responsible for changes in the oceanic carbonate system, with effects on partial pressure of CO_2 (PCO_2), DIC, pH, alkalinity and calcium carbonate saturation state (Feely et al., 2010; Beaufort et al., 2011). In the case of calcifying organisms one observes a marked pattern of decreasing calcification with increasing PCO_2, which follows the corresponding decreasing concentrations of CO_3^{2-} as a consequence of decreasing pH (Beaufort et al., 2011). Such effects finally cause a decline in calcification and growth rates of shellfish (Talmage and Gobler 2010; Wittmann and Pörtner 2013), of shell-forming marine plankton and of benthic organisms including corals (Kleypas et al., 1999; Doney et al., 2009; Beaufort et al., 2011; Pandolfi et al., 2011; McCulloch et al., 2012). The latter have already been lost or are highly damaged in coastal areas near many countries including Indonesia, Hawaii, Caribbean, Fiji, Maldives, and Australia (Erez et al., 2011). A 30% decline or damage of coral reef ecosystems has been estimated worldwide, and it is predicted that as much as 60% of the world's coral reefs might be lost by 2030 (Hughes et al., 2003).

The extent and effects of ocean acidification can be exacerbated by several complex processes, some of which act as stimulating factors, such as local environmental impacts including terrestrial or riverine runoff (Sunda and Cai 2012; Bauer et al., 2013), modified land-use practices (Lapola et al., 2014) and atmospheric acid rain (Baker et al., 2007). An additional effect could be represented by the enhanced mineralization of DOM and PP (*e.g*., phytoplankton) as a consequence of global warming (Mostofa et al., 2013a). Such mineralization could be biological (respiration) or abiotic *via* different (mainly) photochemical processes. Most of the cited effects are expected to cause eutrophication or algal blooms in coastal seawater, which would in turn affect the carbon cycling and the carbonate chemistry and influence the overall acidification process (Beaufort et al., 2011; Sunda and Cai, 2012; Bauer et al., 2013). Such acidification is responsible for changes in the oceanic carbonate system (Feely et al., 2010; Beaufort et al., 2011), which subsequently impacts on marine living organisms and the related ecosystem processes or services (Cooley et al., 2009; Mora et al., 2013; Mostofa et al., 2013a). Considering the possible devastating consequences on the marine ecosystems, their organisms and the related ecosystem services (Cooley et al., 2009; Doney et al., 2009; Cai, 2011; Doney et al., 2012), it is important to ascertain all the possible causes of ocean acidification and their interlinks.

This review will provide a general overview of the ocean acidification, including the interactions between acidification by CO_2 and other processes that could in turn modify the seawater pH. We shall discuss changes in the pH values in both sea surface and subsurface/deeper water extensively with different time scales, from diurnal to multi-annual. We shall also address potential impacts of ocean acidification on marine organisms, along with possible indirect impact processes from a series of stimulating factors (oxidative stress in surface seawater, hypoxia in subsurface/deeper seawater, stress caused by algal or red-tide toxins and pathogens) for both sea surface and subsurface/deeper water. Our review from point of synergistic effects of ocean acidification with such stimulating factors will broaden to understand the potential impact of acidification on biological processes. Such impact is based on the conceptual model provided for both surface and deeper seawaters.

2 Potential mechanisms behind ocean acidification

Ocean acidification includes several potential phenomena that may be operational at the global and/or local scales (Fig. 1): (*i*) Increasing dissolution of atmospheric CO_2 to seawater: Anthropogenic ocean acidification; (*ii*) input of CO_2 plus DIC upon mineralization of PP influenced by elevated atmospheric CO_2: Natural ocean acidification; (*iii*) enhanced PP and respiration due to the effects of global warming and other processes: Natural ocean acidification, and (*iv*) direct acidification and stimulation of PP by atmospheric acid rain: Natural and anthropogenic ocean acidification. A pictorial scheme of the main operational processes affecting the ocean acidification is depicted in Figure 1.

2.1 Increasing dissolution of atmospheric CO_2 to seawater: Anthropogenic ocean acidification

Enhanced dissolution of atmospheric CO_2 to seawater lowers pH and modifies the carbonate chemistry, affecting both biogenic and sedimentary $CaCO_3$. This process has extensively been discussed in earlier reviews (Pearson and Palmer 2000; Feely et al., 2008; Beaufort et al., 2011). For the given seawater, net CO_2 fluxes (either from atmosphere to water or the reverse) may significantly vary depending mostly on time (day or night) and season. Based on a series of studies, six scenarios can be formulated for the net sea-air fluxes of CO_2. They are: (*i*) sinking or balance of atmospheric CO_2 to seawater under sunlight, and emission or balance of CO_2 to the atmosphere during the night; (*ii*) emission or balance of CO_2 to the atmosphere during daytime, and sinking or balance of atmospheric CO_2 to surface water during the night; (*iii*) emission or balance of seawater CO_2 to the atmosphere during both day and night; (*iv*) sinking or balance of atmospheric CO_2 to surface water during both day and night; (*v*) sinking or source or balance of atmospheric CO_2 to surface water during the warm period; and (vi) emission or sinking or balance of seawater CO_2 to the atmosphere during the cold period. These scenarios are described in the supplementary section (see supplementary material).

2.2 Input of CO_2 plus DIC upon mineralization of PP influenced by elevated atmospheric CO_2: Natural ocean acidification

The formation and seawater dissolution of CO_2 and DIC produced from photoinduced and biological mineralization of primary producers (PP) or dissolved organic matter (DOM) also lowers pH and modifies the carbonate chemistry (Fig. 2) (Cai et al., 2006; Feely et al., 2010; Cai et al., 2011; Sunda and Cai 2012; Bates et al., 2013; Mostofa et al., 2013a). Anticorrelation between pH and CO_2 levels during the diurnal cycle has been observed in surface and sub-surface waters (Fig. 2), where CO_2 is mainly originated from the biological respiration of PP or DOM. Such an issue is further complicated by the fact that enhanced levels of CO_2 are partially responsible for the increase of photosynthesis (Behrenfeld et al., 2006; Kranz et al., 2009), and they may have a deep impact on the net primary production (PP) (Hein and Sand-Jensen 1997; Behrenfeld et al., 2006; Jiao et al., 2010). The upper ocean organisms, mostly the autotrophs, are a massive carbon-processing machine that can uptake atmospheric CO_2 (Hein and Sand-Jensen 1997; Falkowski et al., 1998; Sarmento et al., 2010) or CO_2 plus DIC regenerated from DOM or PP, particularly during the daytime (Fig.2a; see also supplementary material) (Takahashi et al., 2002; Yates et al., 2007; Chen and Borges 2009; Takahashi et al., 2009; Mostofa et al., 2013a). In contrast, during the night seawater can become a source of CO_2, as shown in Figure 2 in three different contexts. The ability of water to act as a CO_2 source is shown by the higher values of PCO_2 in seawater compared to that in atmosphere (Zhai et al., 2005; Yates et al., 2007; Chen and Borges 2009; Zhai et al., 2014).

The daytime uptake of CO_2 is the consequence of primary production through photosynthesis, which mostly uses dissolved CO_2 *via* the enzyme ribulosebiphosphate carboxylase (RUBISCO), which governs the carbon-concentrating mechanisms (CCMs)

(Yoshioka 1997; Behrenfeld et al., 2006; Kranz et al., 2009). Mesocosm experiments using ^{14}C-bottle incubations indicate that elevated CO_2 can increase ^{14}C-primary production or bacterial biomass production, also leading to the formation of dissolved organic carbon (DOC) and to its rapid utilization (Engel et al., 2012). Photosynthetic carbon fixation by marine phytoplankton leads to the formation of ~45 gigatons of organic carbon per annum, of which 16 gigatons (~35.6% of the total) are exported to the ocean depths (Falkowski et al., 1998). Furthermore, all primary producers including the large and small cells can contribute to the carbon export from the surface layer of the ocean, at rates proportional to their production rates (Richardson and Jackson, 2007). The reprocessing of this organic material can cause a decrease in the pH of seawater *via* the CO_2 produced by respiration (Jiao et al., 2010). If, in addition, organic N and P are biologically transformed into NO_3^- and phosphate (Mostofa et al., 2013a) and if there is also transformation of NH_4^+ to N_2 (Doney et al., 2007), there can be a further decrease of seawater alkalinity. Such processes also decrease the buffering capacity of seawater (Thomas et al., 2009), which would become more susceptible to acidification caused by the dissolution of atmospheric CO_2 (Thomas et al., 2009; Cai et al., 2011). A decrease in alkalinity and accompanying acidification may have negative impacts on shellfish production (Hu et al., 2015).

Heterotrophic bacteria are the main organisms that are responsible for respiration in the ocean (> 95%) (Del Giorgio and Duarte, 2002), and half of the respiration (approximately 37 Gt of C per year) takes place in the euphotic layer (del Giorgio and Williams 2005). An interesting issue is that such bacteria are also important sources of the superoxide radical anion ($O_2^{-\bullet}$) (Diaz et al., 2013), the dismutation of which (2 $O_2^{-\bullet}$ +

$2\ H^+ \rightarrow H_2O_2 + O_2$) consumes H^+ and could partially buffer at local scale the acidification that is connected to the degradation of OM (Mostofa et al., 2013b).

The biological transformation of DOM and PP is active constantly at the sea surface as well as in the subsurface/deeper water, whilst photoinduced degradation is merely active during daytime in the sea surface layer. Of course, such processes show variations associated with seasonal and annual changes in deep-sea geochemistry and biology, along with phenomena associated with ocean circulation (Asper et al., 1992; Thomas et al., 2004). The entire phytoplankton biomass of the global oceans is consumed every two to six days (Behrenfeld and Falkowski, 1997) and part of the carbon fixed by the autotrophs is actually respired *in situ* (Sarmento et al., 2010), also providing nutrients for the microbial food web (Behrenfeld et al., 2006; Sarmento et al., 2010). In some cases, the reprocessing of nutrients is involved in harmful algal blooms or eutrophication by enhanced photosynthesis in surface seawater (Sunda and Cai 2012; Mostofa et al., 2013a).

2.3 Enhanced PP and respiration due to the effects of global warming and other processes: Natural ocean acidification

Anthropogenic global warming could also enhance the natural acidification process. The dissolution of $CO_{2(g)}$ and DIC released from PP and its subsequent respiration/degradation can be enhanced by the effects of GW (Behrenfeld et al., 2006; Cai et al., 2006; Kranz et al., 2009; Cai et al., 2011; Sunda and Cai 2012; Mostofa et al., 2013a; Holding et al., 2015). GW is a key factor to increase water temperature (WT), which can affect the extent and the duration of the vertical stratification during the summer season. Furthermore, the prolonged exposure of the surface water layer to sunlight may cause photoinduced bleaching of sunlight-absorbing DOM, the so-called Color Dissolved Organic Matter (CDOM), thereby enhancing the water column transparency and modifying the depth of the mixing layer or euphotic zone (Behrenfeld et al., 2006; Huisman et al., 2006). The increased stability of the water column may also enhance the photoinduced and biological mineralization of OM, due to the combination of higher temperature and of the longer exposure of the water surface layer to sunlight (Huisman et al., 2006; Vázquez-Domínguez et al., 2007). A further effect is the reduction of subsurface dissolved O_2 because of the decline of vertical winter mixing, which subsequently reduces the exchange of surface oxygenated water to the deeper layers (Fig. 1). Increasing temperature increases the respiration rates in natural waters (Vázquez-Domínguez et al., 2007), and it affects phytoplankton metabolism nearly as significantly as nutrients and light do (Toseland et al., 2013). Various photoinduced and microbial products/compounds formed from DOM or PP [*e.g.* CO_2, DIC, H_2O_2, NH_4^+, NO_3^-, PO_4^{3-}, CH_4, autochthonous DOM], the generation of which can be higher in stratified surface water as a consequence of GW, may enhance photosynthesis and, consequently, primary production as schematized in supplementary Figure 1 (Bates and Mathis, 2009; Cai et al., 2011; Mostofa et al., 2013a). Further details are reported in the Supplementary Material.

3 Diurnal, abrupt and homogeneous pH changes in seawater

In some locations, the pH of the sea surface water gradually increases during the period before sunrise to noon and then decreases after sunset as a function of the solar irradiation flux (Fig. 3a-b) (Fransson et al., 2004b; Arakaki et al., 2005; Akhand et al., 2013). Furthermore, substantial fluctuations of the pH values during daytime are also observed (Fig. 3a-b) (Fransson et al., 2004a; Arakaki et al., 2005; Clark et al., 2010). The magnitude of the diurnal pH variation can be substantial, ranging from ~0.01 in waters with low biological activity to 1.60 in waters with high biological activity that are influenced by riverine inputs, particularly in coastal areas (supplementary Table 1). More specifically, pH has been observed to increase by 0.03 to 0.81 units in surface coastal seawater, from 0.26 to 1.60 in macroalgae, 0.01 to 0.75 in coral reefs, from 0.17 to >1.00 in the seagrass community, from 0.03 to 1.59 in CO_2 venting sites, and from 0.04 to 0.10 in polar oceans (supplementary Table 1) (Semesi et al., 2009; Taguchi and Fujiwara 2010; Hofmann et al., 2011). Diurnal pH changes in sea surface waters are apparently triggered by two phenomena. The first and key issue is the consumption or dissolution in seawater of CO_2 that is involved in primary production (Fig. 2a-b) (Akhand et al., 2013; Zhai et al., 2014). Depending on the ratio between photosynthesis and respiration, diurnal fluctuations of PCO_2 are observed in seawater and the PCO_2 maxima correspond to pH minima and *vice versa*. In the case of Figure 2a,b the pH maxima are observed at noon or soon after noon; in other locations they may occur in different times of the day, but the anticorrelation between pH and PCO_2 is always observed. At the sea surface one may observe a diurnal decrease in PCO_2 with an increase in pH during the day time or in the presence of sunlight (due to the prevalence of photosynthesis), along with an increase in PCO_2 with decrease in pH at night when respiration prevails (Yates et al., 2007; Semesi et al., 2009).

A second issue that might affect pH is the photoinduced generation of H_2O_2, primarily by dismutation of superoxide radical anion ($2O_2^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2$) (Fig. 3a-b)

(Arakaki et al., 2005; Clark et al., 2010) and the subsequent production of the strong oxidant, hydroxyl radicals ($HO^{\bullet}$) *via* photolysis or Fenton and photo-Fenton processes, which are responsible for the degradation of DOM and POM (Vione et al., 2006; Minakata et al., 2009). The linear correlation between pH / [H_2O_2] and the UV intensity (Fig. 3c-d) can be elucidated by considering that both variables are directly influenced by solar irradiation.

Seawater pH is predominantly determined by the balance between consumption (photosynthesis) and release (respiration) of CO_2 as a consequence of the PP activity. In the reported cases the maximum consumption of dissolved CO_2 takes place at the same time of the maximum activity of the photo-stimulated biota. In addition, the positive correlation between [H_2O_2] and UV intensity (Fig. 3c-d) is linked to the fact that the $O_2^{-\bullet}$ production rate overlaps with the maximum of solar irradiation, because the biological and photochemical production of $O_2^{-\bullet}$ is activated by light absorption. The concentration of H_2O_2 in sea surface water gradually increases during the period before sunrise to noon and then decreases after sunset as a function of solar irradiation (Fig. 3a-b). The amplitude of the H_2O_2 diurnal cycle (highest concentration at noon time minus concentration during the period before sunrise) ranged from 20 to 365 nM in coastal seas to marine bathing waters (supplementary Table 1). Both the $O_2^{-\bullet}$ production and its dismutation with formation of H_2O_2 involve H^+ exchange and can consequently affect the ocean pH. $O_2^{-\bullet}$ is largely produced by the enzyme NADPH oxidase through the synthesis of $HO_2^{\bullet}$ that is a weak acid (*pKa*= 4.88) (Bielski et al., 1985), which dissociates at the oceanic pH releasing H^+ ions according to the following reactions

$$O_2 + NADPH \rightarrow NADP + HO_2^{\bullet} \qquad \text{eq. 1}$$

$$HO_2^{\bullet} \leftrightarrows O_2^{-\bullet} + H^+ \qquad \text{eq. 2}$$

The production and dismutation of $O_2^{-\bullet}$ is a H^+-neutral process, but the fate of the superoxide anion is also a consequence of the redox state of the environment. Indeed, superoxide can be oxidized to O_2 ($O_2^{-\bullet} \rightarrow O_2 + e^-$) or reduced to H_2O_2 ($O_2^{-\bullet} + e^- + H^+ \rightarrow H_2O_2$). The prevalence of one of the two processes may not have the same effect on the overall H^+ budget and can consequently affect the acid-base equilibria of oceanic seawater. The generation of $O_2^{-\bullet}$ and consequently of H_2O_2 (Fig. 3a-b) would give an additional contribution to the daytime pH maxima and, as a consequence, could be a further actor in the definition of the daytime pH fluctuation.

Apart from the diurnal cycle, abrupt pH changes caused by both photoinduced and biological processes (overlapping to diurnal changes) have been observed in surface seawater and among the branches of *Pocillopora*colonies in the Great Barrier Reef (Gagliano et al., 2010), in the surface seawater of Okinawa Island (Fig. 3a,b) (Arakaki et al., 2005), in marine bathing waters (Southern California) (Clark et al., 2010), in the North Sea (Blackford and Gilbert 2007), in the North Pacific Ocean (Byrne et al., 2010), in the Chwaka Bay (Semesi et al., 2009) and in the northeast Atlantic (Findlay et al., 2014). Such rapid changes in pH are supposed to be a consequence of the primary production as well, although the details of the pH-modifying pathway(s) are still poorly understood. Proposals include several processes in which an intracellular microenvironment is produced, with very different pH values compared to the surrounding seawater, with possible release of intracellular material as a consequence of *e.g.* cell lysis. Among these processes the main are: (*i*) pH variation connected with aggregates present in photosynthetically active cells or inside colonies (Lubbers et al., 1990); (ii) polyanion-mediated formation of mineral–polymer composites inside alginate microgels or in the Golgi of coccolithophorid algae (Chin et al., 1998); (iii) processes occurring at the site of calcification such as conventional H^+-channeling, Ca^{2+}–H^+ exchanging ATPase, transcellular symporter and co-transporter H^+-solute shuttling(Ries 2011); (iv) cellular extrusion of hydroxyl ions (OH^-) into the calcifying medium (Ries 2011); and (*v*) CO_2-consumption via photosynthesis (Ries, 2011). By the way, the ability to up-regulate pH at the site of calcification can provide corals with enhanced resilience to the effects of ocean acidification (McCulloch et al., 2012). Increased pH during high primary productivity can be justified by the observation of a parallel increase in the $\delta^{13}C$ values of POM, which may reflect a shift by phytoplankton from using CO_2 to using HCO_3^- for photosynthesis (Doi et al., 2006; Akhand et al., 2013). Therefore, uptake of HCO_3^- for phytoplankton photosynthesis at high pH might be the effect of its enhanced occurrence in seawater.

Homogeneous (longer-term and constant-rate) acidification in subsurface/deeper seawater is characteristically observed in oceans (Fig. 2c and supplementary Table 1; Feely et al., 2008; Byrne et al., 2010; Taguchi and Fujiwara, 2010; Cai et al., 2011; Zhai et al., 2012; Bates et al., 2013), estuaries (Feely et al., 2010), and experimentally in dark incubation (Lubbers et al., 1990). Such a homogeneous pH behavior is also followed in the subsurface water of a large freshwater lake (supplementary Figure 2a). At the beginning of the summer stratification period, pH in subsurface water (at depths of 40 and 80 m) gradually decreases whilst pH in the surface lake water (at depths of 2.5 and 10 m) increases, while dissolved organic carbon (DOC, Supplementary Figure 2b) and PP (chlorophyll *a*, Supplementary Figure 2c) also increase. Similar results, particularly monthly pH variations in surface and deeper seawater, are observed in the Seto Inland Sea during the summer stratification period and during convective mixing periods (Taguchi and Fujiwara, 2010). Homogeneous acidification can vary on a time scale of days to weeks or even months in a wide range of subsurface water at a specific depth (Supplementary Figure 3; Byrne et al., 2010; Taguchi and Fujiwara, 2010). For example, pH was 7.4 at ~ 2000-2500 m depth and 7.5 at ~2500-3400 m depth along with 25°N to 55°N on North Pacific Ocean (Byrne et al., 2010), or pH was 7.0 at 80 m depth during the August-November period (Supplementary Figure 3). In the dark, pH decreases gradually inside colonies and also 'nightly' decreases of pH occur (Lubbers et al., 1990). Such homogenerous acidification is primarily linked to the dissolution of CO_2 plus DIC originated from the biological degradation of sinking microorganisms (Bates and Mathis, 2009; Cai et al., 2011) and of the DOM originally produced by such organisms (Mostofa et al., 2013a). Enhanced acidification due to the biological degradation of OM can cause undersaturation of aragonite and calcite during the summer period in subsurface/deeper seawater in the Yellow Sea (Figs. 2b, 4) (Zhai et al., 2013), Gulf of Mexico (Cai et al., 2011; Sunda and Cai, 2012), North Pacific Ocean (Byrne et al., 2010), Artic Ocean (Bates et al., 2013), and Arctic shelves (Bates and Mathis, 2009).

The biological degradation processes are constantly occurring in subsurface/deeper seawater after the onset of early summer, and they continue during the summer stratification period for several months, until the start of winter vertical mixing (Fig. 1). The occurrence and importance of these processes is shown by the increasing trend in subsurface CO_2 followed by a similar decreasing trend of pH. Significant anticorrelation between the two parameters ($r^2 = 0.5$) has been observed in subsurface seawater (13-75 m depth) along 37°25ʻ-39°67ʻ N to 121°16ʻ -124°10ʻ E in the Yellow Sea (Fig. 4a). Furthermore, the same evidence was observed in the Seto Inland Sea (Taguchi and Fujiwara, 2010) and in the diurnal samples 8 of Luhuitou fringing reef (Sanya Bay) of South China Sea (Zhang et al., 2013). Strong anticorrelation between $PCO_{2[seawater]}$ and dissolved O_2 ($r^2 = 0.8$; Fig. 4b) supports the production of CO_2 plus DIC from the biological respiration/degradation of DOM and PP by heterotrophic bacteria as discussed earlier. Such bacteria also produce the superoxide radical anion ($O_2^{\bullet -}$) (Diaz et al., 2013) that might be further involved in the processing/oxidation of DOM or PP by producing H_2O_2 and consequently $^{\bullet}OH$ via photolysis, photo-Fenton or Fenton-like processes. Such trends of CO_2 (or DIC) *vs.* dissolved O_2 are also observed in California coastal waters (DeGrandpre et al., 1998), in East China Sea (Zhai and Dai, 2009), in South China Sea (Zhai et al., 2009), and in Seto Inland Sea (Taguchi and Fujiwara, 2010). Biological respiration can be evidenced from an experiment conducted using subsurface water (37 m depth) collected from East China Sea, where the decline in dissolved O_2 is significantly coupled with an increase of DIC production during a 60-hours study period (Fig. 4c). The heterotrophic bacteria carry out the largest fraction of respiration (> 95%) in the ocean (Del Giorgio and Duarte, 2002). This means that the heterotrophic community catabolizes an important percentage of the OM produced by the autotrophs (*e.g*. plants, algae or bacteria) (Laws et al., 2000). Therefore, enhanced primary production or algal blooms in surface seawater and the subsequent sinking are the key processes for homogeneous acidification of the subsurface layer during the summer stratification period, through the degradation of sinking organic material. Finally, different regions or ecosystems are expected to give different responses to ocean acidification (Gattuso et al., 2015). Unfortunately, little has been documented on geographical comparisons on this aspect.

4 Possible forthcoming impacts on ocean acidification

An increase in world population (9 billions estimated at 2050) with increasing needs of energy, food, medicines and habitats is one of the key issues (Mostofa et al., 2013a) that will probably contribute not only to the increase of atmospheric CO_2, but also to the exacerbation of other factors that may also be related to ocean acidification. Such factors include enhanced photosynthesis (because of the release of terrestrial OM and nutrients from increased land use), the increment of OM and nutrients in wastewater, acid rain, and so on. The following issues can be foreseen in the next decades, unless remedial actions of some sort are taken:

(i) Long-term homogenous acidification in the deeper waters of both coastal and oligotrophic oceans, apparently caused by biological respiration of DOM and PP and their subsequent release of CO_2 or DIC, could have key impacts on marine organisms (Cai et al., 2011; Bate et al., 2013; Zhai et al., 2013; Byrne et al., 2010; Zhai et al., 2014; Mostofa et al., 2013). Such homogenous effects of acidification are directly linked to the effects of GW that can enhance the surface water temperature. The consequence is an extension of the summer stratification period, which would determine acidification in deeper oceans.

(ii) Coastal seawater, particularly in locations that are highly influenced by terrestrial river freshwater inputs, is at risk of substantial acidification, to a higher extent compared to the open oceans (Zhai et al., 2014; Thomas et al., 2009; Bate et al., 2013; Barton et al., 2014; Cai et al., 2011; Cai, 2011; Bauer et al., 2013; Hu et al., 2015). In fact, in addition to the dissolution of atmospheric CO_2, coastal seawater would be subjected to acidification processes connected with eutrophication, acid rain and pollution-affected respiration (Doney et al., 2007; Cai et al., 2011; Sunda and Cai 2012; Zeng et al., 2015). Indeed, OM is substantially increasing in coastal oceans (Bauer et al., 2013). Furthermore, transport phenomena (*e.g.* oceanic

pump) will gradually increase the level of nutrients, DOM and PP from coastal areas in the direction of the oligotrophic open ocean (Fig. 1) (Thomas et al., 2004). Therefore, additional acidification processes in the oligotrophic open ocean could be operational and more significant in the coming decades.

(iii) Enhanced PP and respiration could increase PCO_2 in open-ocean water and decrease the ability of seawater itself to act as a sink of atmospheric CO_2. The consequence will be an extension of the zones where seawater acts as a source of CO_2, which has increased at an average rate of 1.5 µatm y^{-1} in 1970-2007 (Takahashi et al., 2002; Takahashi et al., 2009). In addition to the contribution to ocean acidification, the decreasing ability of seawater to act as CO_2 sink will also exacerbate the problems related to GW.

(iv) The present sea-air fluxes of CO_2 (Takahashi et al., 2009) suggest that the equatorial oceans are prevailingly a CO_2 source to the atmosphere while the temperate ones are mainly a sink. Figure 5 reports the predicted pH changes by 2100 (Mora et al., 2013), showing that acidification is expected to affect all the world's oceans but that the most important effects are predicted for the elevated northern and southern latitudes. Such locations are presently the sites that mostly act as CO_2 sinks, because seawater PCO_2 is lower than the atmospheric one, and they will experience the most important pH-associated increase of seawater PCO_2. It is thus likely that the global map of sea-air CO_2 fluxes will undergo important changes during the 21st century.

5 Impacts of acidification on marine organisms

Marine organisms at low and high latitudes do not respond uniformly to ocean acidification (Hendriks et al., 2010; Toseland et al., 2013), and the expected effects can thus be stimulative, inhibitive, or neutral (Anthony et al., 2008; Gao et al., 2012a; Hutchins et al., 2013). Considering the overall processes that are involved in ocean acidification (see Fig. 1), it can be assumed that marine organisms would face detrimental impacts under the following conditions: *(i)* they are peculiarly susceptible to pH changes with different time scales and particularly to acidification, which applies for instance to the majority of marine calcifiers; (*ii*) they live under hypoxia in long-term homogeneous acidified subsurface/deeper seawater, where they cannot carry out respiration and metabolism properly (this would happen during a stratification period of increasing duration due to GW, which can damage their natural growth and development); and (*iii*) they are subjected to death/damage in surface seawater by the action of algal toxins and pathogens (*e.g*. viruses, coliform bacteria, fungi), and/or to oxidative stress caused by reactive oxygen species (ROS) and increased water temperature. In many cases it is extremely difficult (or even next to impossible) to disentangle acidification from other processes that are taking place at the same time. Actually, the impacts of increasing acidification on marine organisms may derive from several processes that are closely interlinked: *(i)* acidification; *(ii)* synergistic effects of acidification and oxidative stress in surface seawater; *(iii)* low dissolved O_2 (hypoxia) and acidification in subsurface/deeper seawater, and *(iv)* stress by algal or red-tide toxins and pathogens.

5.1 Acidification

Impacts induced by seawater acidification or reduced seawater pH are recognized phenomena and they are discussed in many early reviews. However, seawater acidification or reduced seawater pH may produce undersaturation of aragonite and calcite, with the following effects in a variety of seawaters: (*i*) dissolution of biogenic shells or skeletons, mostly composed of $CaCO_3$ in the forms of calcite or aragonite, of adult marine calcifiers such as corals (Kleypas et al., 1999; Erez et al., 2011; Pandolfi et al., 2011; Wittmann and Pörtner, 2013), crustose coralline algae (Anthony et al., 2008; Hall-Spencer et al., 2008), shellfish (Talmage and Gobler, 2010; Barton et al., 2012; Wittmann and Pörtner, 2013), marine plankton including foraminifera,(De Moel et al., 2009; Moy et al., 2009) and coccolithophores (Riebesell et al., 2000; Beaufort et al., 2011), mollusks (Doney et al., 2009; Wittmann and Pörtner, 2013) and echinoderms (Doney et al., 2009; Wittmann and Pörtner, 2013); sedimentary $CaCO_3$ would be affected as well (Kleypas et al., 1999; Bates et al., 2013); (*ii*) inability to form new shells or skeletons of framework builders by larvae or juvenile calcifiers (*e.g*. the larval and juvenile stages or smaller individuals), particularly at the early development stages. The effect would be operational through the decline of calcification rates, which substantially decreases the growth and development of the organisms including corals (Kleypas et al., 1999; Anthony et al., 2008; Kroeker et al., 2013); and (*iii*) ocean acidification could indirectly enhance heterotrophic bacterial activities with increasing bacterial protein production and growth rate at elevated pCO_2 levels (Grossart et al., 2006; Endres et al., 2014; Baragi et al., 2015); higher bacterial abundance has been reported under high pCO_2 treatments (Endres et al., 2014; Tait et al., 2013), which could consequently accelerate respiration processes and increase the respiratory CO_2 production in the future ocean

(Piontek et al., 2010). As discussed in section 3, seawater pH varies in different time scales and shows short-term variations (*e.g*. minutes to hours: diurnal and abrupt) in upper surface seawater and long-term variations (*e.g*. weeks to several months: homogeneous) in subsurface and deeper seawater. Long-term homogenous acidification is apparently responsible for the majority of impacts on marine organisms. However, the impact on marine calcifiers of pH variations in different time scales, and most notably the diurnal ones, is presently poorly known and should be the focus of future research.

5.2 Synergistic effects of acidification and oxidative stress in surface seawater

The rapidly rising levels of atmospheric CO_2 will result in ocean warming in addition to lowering the seawater pH (Solomon et al., 2009; McCulloch et al., 2012). Marine calcifiers are for instance more sensitive to increased temperature under low pH conditions, because of the combination of two stressors (Wood et al., 2010; Pandolfi et al., 2011; Hiebenthal et al., 2013; Kroeker et al., 2013). The synergistic effects of ocean acidification and oxidative stress, elevated water temperature or high irradiance, all connected with increasing CO_2 and GW, can affect marine ecosystems to a variable degree. In some cases the marine primary productivity is decreased (Boyce et al., 2010; Gao et al., 2012a), while in other cases the decrease is not so obvious as tolerance to elevated CO_2 levels may be developed (Feng et al., 2009; Gao et al., 2009; Connell and Russell 2010). However, even in the latter instances one may observe deep changes in species composition (Meron et al., 2011; Witt et al., 2011), and sometimes even an increase in coral productivity in experimental studies (Anthony et al., 2008). However, a drop in biodiversity is generally observed that is always to the detriment of calcifying organisms (Hall-Spencer et al., 2008; Connell and Russell, 2010). The observed negative effects include bleaching and productivity loss in coral reef builders (Hoegh-Guldberg et al., 2007; Anthony et al., 2008), high mortality and reduction of shell growth and shell breaking force (Hobbs and McDonald, 2010; Lischka et al., 2010; Hiebenthal et al., 2013), declining calcification and enhanced dissolution (Rodolfo-Metalpa et al., 2010), decline in abundance of the juveniles population (Lischka et al., 2010), and increased N:P ratios of eukaryotic phytoplankton (Toseland et al., 2013).

The mechanism behind the oxidative stress at elevated WT or high irradiance is caused by a substantial generation of ROS, such as $O_2^{\bullet -}$, H_2O_2, $HO^{\bullet}$ or $^1O_2$, in the surface water layer. The hydroxyl radical ($HO^{\bullet}$), a strong oxidizing agent, is produced from either endogenic or exogenic H_2O_2 through Fenton and photo-Fenton reactions in the presence of metal ions, and upon photolysis of NO_2^- or NO_3^- (Zepp et al., 1992; Mostofa et al., 2013c; Gligorovski et al., 2005). Inside organisms, $HO^{\bullet}$ can damage the photosystem II activities and finally cause cell death (Blokhina et al., 2003; Mostofa et al., 2013c). H_2O_2 concentration levels of approximately 100 nM (compared to up to 1700 nM values that have been detected in coastal waters) (Mostofa et al., 2013c) can cause oxidative stress to bacteria, as determined on the basis of increasing catalase enzyme concentration (Angel et al., 1999). H_2O_2 can also reduce bacterial abundances by inducing elevated mortality in seawater (Clark et al., 2008). The oxidative stress that is related to the Fenton processes would even increase in acidified water, where the $HO^{\bullet}$ yield is higher (Zepp et al., 1992). Interestingly and coherently with the expected $HO^{\bullet}$ yield, the degree of oxidative stress in mollusks has been found to increase with decreasing pH (Tomanek et al., 2011), and the pH effect is further exacerbated by an increase in temperature (Matozzo et al., 2013). Furthermore, the synergistic effect of high H_2O_2 combined with high seawater temperature resulted in a 134% increase in coral metabolism/respiration rates (Higuchi et al., 2009).

Moreover, one should not only focus on the direct detrimental effects at the organism or single-species level: the negative impacts on the dynamics, structure, composition and biodiversity of the coral reefs (Findlay et al., 2010; Wittmann and Pörtner 2013), of other marine calcifiers (Feng et al., 2009; Wittmann and Pörtner 2013) and of marine ecosystem processes would be linked to changes in species abundance, distribution, predator vulnerability and competitive fitness (Hiscock et al., 2004; Feng et al., 2009; Gao et al., 2012b).

5.3 Synergistic effects of low dissolved O_2 (hypoxia) and acidification in subsurface/deeper seawater

Declining dissolved O_2 in deeper seawater would mostly be caused by reduced vertical mixing as a consequence of GW (Huisman et al., 2006; Keeling et al., 2010), which inhibits reoxygenation while O_2 in deep water is consumed by biological respiration/degradation of sinking organisms and DOM (Fig. 1) (Stramma et al., 2008; Cai et al., 2011; Sunda and Cai 2012; Zhai et al., 2012; Mostofa et al., 2013a). The key reason for hypoxia is the long-term biological respiration/degradation of sinking OM in the absence of mixing, which is also a key pathway for acidification in sea subsurface water during the summer stratification period, as is discussed in earlier sections. The net decrease of dissolved O_2 in subsurface seawater in the Bohai Sea (China) between June and August 2011was 34-62% (see supplementary Fig.3a), which would be the result of OM respiration during the summer stratification period. The hypoxia in subsurface water (40 and 70-80 m depths) (supplementary Fig.3b) along with changes in pH, DOC and primary producers (PP) or Chl*a* (supplementary Figure 2) is linked with enhanced sinking of PP at the end of the summer stratification period. The connection between hypoxia (through respiration of OM) and acidification can be assessed by the positive correlation between pH and dissolved O_2 (supplementary Fig. 4), which shows that declining O_2 is directly associated with reduced pH in subsurface/deeper seawaters (supplementary Fig. 4; Cai et al., 2011; Zhai et al., 2012; Zhang et al., 2013).The connection between hypoxia and acidification could be exacerbated, and long-term hypoxia could be induced, by two important factors, namely (*i*) the increase in algal blooms and the subsequently enhanced sinking of dead algae in subsurface/deeper seawater, and (*ii*) the effects of GW that would induce longer stratification periods as a consequence of a longer summer season, as previously discussed.

Recent study reveals that hypoxia and acidification have synergistic detrimental effects on living organisms, because they can separately affect growth and mortality and their combination can cause damage to organisms that are resistant to the separate stresses (Gobler et al., 2014). Moreover, acidification can cause an additional worsening of survival conditions in oxygen-poor waters, which are already made more acidic by the degradation of OM (Melzner et al., 2013). The overall consequences of hypoxia and acidification affect the natural growth and development of organisms (Boyce et al., 2010) and have implications for habitat loss (Keeling et al., 2010; Stramma et al., 2010), fish mortality (Hobbs and McDonald, 2010), nutrient cycling (Keeling et al., 2010; Toseland et al., 2013), carbon cycling (Keeling et al., 2010), ecosystem functioning (Diaz and Rosenberg, 2008) and diversity, with possible changes of species composition in the bentho-pelagic communities (Diaz and Rosenberg, 2008; Stramma et al., 2010).

5.4 Stress caused by algal or red-tide toxins and pathogens

Ocean acidification or elevated CO_2 could increase the toxic algal blooms, involving for instance the diazotrophic cyanobacterium *Nodularia spumigena* (Endres et al., 2013; Olli et al., 2015). They could also increase the accumulation of toxic phenolic compounds across trophic levels in phytoplankton grown under elevated CO_2 concentrations (Jin et al., 2015). Ocean acidification combined with nutrient limitation or temperature changes could considerably enhance the toxicity of some harmful groups (Fu et al., 2012). Correspondingly, harmful algal blooms are expected to increase in coastal waters because of increasing WT and eutrophication (Anderson et al., 2008; Glibert et al., 2010; Mostofa et al., 2013a), which would enhance net primary productivity that is the essential backdrop for the development of such blooms. The same phenomena are also involved in acidification, thus it can be expected that more frequent algal blooms will take place along with ongoing acidification as an additional stress to marine organisms. Algal blooms and acidification could also be more closely linked (Cai et al., 2011; Sunda and Cai, 2012), because the decline of marine algae with a calcareous skeleton could produce a selective advantage for harmful species (Irigoien et al., 2005; Mostofa et al., 2013a).

Harmful algal blooms can produce algal toxins (*e.g*. microcystins) or red-tide toxins (*e.g.*, brevetoxins) (Flewelling et al., 2005; Anderson et al., 2008), and the occurrence of pathogens (*e.g*. potentially hazardous fecal-oral viruses, coliform bacteria, parasites, or fungi) (Littler and Littler, 1995; Suttle, 2005) is also more likely in the presence of large phytoplankton cells and during algal blooms (Fuhrman, 1999; Suttle, 2005). Toxins and pathogens are a major cause of morbidity and mortality for marine organisms and they can affect humans as well (Harvell et al., 1999; Flewelling et al., 2005; Anderson et al., 2008). The most common toxins are microcystins, cyanotoxins (blue green algal toxins), okadaic acid (OA), dinophysis toxins (DTXs) and pectenotoxins (PTXs) produced by dinoflagellates (Takahashi et al., 2007), domoic acid (DA) produced by diatoms (Takahashi et al., 2007), and brevetoxins produced by the 'red tide' dinoflagellate *Kareniabrevis* (Flewelling et al., 2005; Anderson et al., 2008). Brevetoxins are potent neurotoxins that kill vast numbers of fish and even large marine mammals: for instance, 34 endangered Florida manatees (*Trichechus manatuslatirostris*) died in southwest Florida in the spring of 2002, and 107 bottlenose dolphins (*Tursiops truncatus*) died in waters off the Florida panhandle in the spring of 2004 as a consequence of exposure to brevetoxins (Flewelling et al., 2005). Furthermore, brevetoxins cause illness in humans who ingest contaminated filter-feeding shellfish or inhale toxic aerosols (Flewelling et al., 2005).

Ocean acidification/elevated CO_2 could indirectly affect bacterial activity and abundance (see section 5.1; Grossart et al., 2006; Allgaier et al., 2008; Endres et al., 2014; Baragi et al., 2015; Witt et al., 2011; Tait et al., 2013). However, the abundance of different bacterial communities could respond differently (increase, remain unchanged or even decrease) under the effect of global warming (Allgaier et al., 2008; Witt et al., 2011; Baragi et al., 2015). However, acidification is also connected to an increase of pathogenic microbiota in corals (Meron et al., 2011). The latter effect is particularly alarming, because coral reefs are already directly endangered by acidification (inhibition of the calcification process, as already discussed) and GW. The reduction in reef-building coral species would be exacerbated by 18 coral diseases identified so far, with increasing prevalence and virulence in most marine taxa (Sutherland et al., 2004). The most concerning diseases are: the black band disease (BBD), probably caused by several species of cyanobacteria including most notably *Phormidium corallyticum* (Rudnick and Ferrari, 1999); the coralline lethal orange disease (CLOD, a bacterial disease affecting coralline algae), which impacts greatly on coral reefs and reef-building processes (Rudnick and Ferrari, 1999); a virulent disease known as white plague type II, which caused widespread mortality in most Caribbean coral species through physical contact with the macroalga *Halimeda opuntia* (Nugues et al., 2004) and, finally, corals bleaching or disease caused by the temperature-dependent bacteria *Vibrio shiloi* (Vidal-Dupiol et al., 2011). Further proposed pathogens for BBD, in addition to *Phormidium corallyticum*, include different genera of cyanobacteria, sulfate-reducing bacteria including *Desulfovibrio* spp., sulfide-oxidizing bacteria presumed to be *Beggiatoa* spp., several other heterotrophs, and marine fungi (Sekar et al., 2006). Any bacterial community shifted by elevated CO_2 could thus impact on other marine organisms. Finally, more experimental researches are warranted to find out links and mechanisms between harmful algal blooms and ocean acidification/elevated CO_2.

6 Potential ecological and biogeochemical consequences arising from future ocean acidification

An overview of the potential upcoming ecological and biogeochemical consequences, linking different environmental drivers, processes and cycles related to acidification in the future ocean is provided in Figure 6. Recent study demonstrated that different types of tropical cyclones (hurricanes and typhoons) could increase significantly in oceans and on land over the 21st century (Lin and Emanuel, 2016). Extreme daily rainfall is thought to increase with temperature in some regions (Chan et al., 2016 and reference therein). Watersheds with high precipitation induce higher riverine discharge rates (Bauer et al., 2013) and, for instance, a single tropical storm can export approximately 43% of the average annual riverine DOC (Yoon and Raymond, 2012). Similarly, on decadal timescales, single large, cyclone-induced floods can transport 77–92% of particulate organic carbon from mountainous regions (Hilton et al., 2008). Correspondingly, enhanced human activities due to increasing population will unquestionably jeopardize Earth's natural systems. Soil erosion is gradually intensified in regions where forests are converted into croplands (Ito, 2007), and humans have increased the sediment transport by global rivers through soil erosion by 2.3±0.6 billion metric tons per year (Syvitski et al., 2005). Potential changes in erosion rates in the Midwestern United States under climate change is predicted and runoff could increase from +10% to +310% (along with soil loss increase from +33% to +274%) in 2040–2059 relative to 1990–1999 (O'Neal et al., 2005). The transfer of OM or organic carbon from the terrestrial soil to the oceans via erosion and riverine transport could significantly affect the coastal oceans (Hilton et al., 2008; Bauer et al., 2013; Galy et al., 2015). Particulate organic carbon (POC) export from the terrestrial biosphere into the oceans is mostly controlled by physical erosion, which is thus predicted to become the dominant long-term atmospheric CO_2 sink under a fourfold increase in global physical erosion rate at constant temperature (Galy et al., 2015).

Such enhanced input of OM with raising temperature under future global warming conditions will drastically impact on the ocean acidification that is concomitantly linked with other biogeochemical processes (Jin et al., 2015; Mora et al., 2013). Moreover, temperature regulates important abiotic and biotic processes that can alter water throughput, flow paths, dissolution rates and watershed carbon stocks (Bauer et al., 2013) as well as stratification period or euphotic zone (Fig. 1; Mora et al., 2013; Huisman et al., 2006; Jöhnk et al., 2008). In addition, elevated temperature under global warming conditions could potentially enhance the proliferation of harmful Cyanobacteria in surface water (Paerl and Huisman, 2008; Jöhnk et al., 2008). The overall ecological and biogeochemical consequences of future ocean acidification under forthcoming global warming conditions in oceans could severely impact on coastal seas, with a spreading of anoxic dead zones and a frequent occurrence of toxic dinoflagellate blooms (Jackson, 2008). Possible evolutions could involve expanding hypoxia in the deeper water layers (Wannicke et al., 2012; Stramma et al., 2008); changes in food-web dynamics (Fabry et al., 2008; Wannicke et al., 2012); changes in the biogeochemical cycling dynamics of C, N, and P (Keeling et al., 2010; Wannicke et al., 2012; Toseland et al., 2013; Unger et al., 2013; Olli et al., 2015; Baragi et al., 2015); changes in metabolic pathways (Jin et al., 2015); increases in coral susceptibility to disease, pathogen abundance and pathogen virulence (Maynard et al., 2015); negative consequences up to mortality for various marine organisms, particularly for the shell-forming ones (Haigh et al., 2015; Doney et al., 2009); structural changes in phytoplankton communities (Dutkiewicz et al., 2015) and in some marine keystone species (Waldbusser et al., 2014; Barton et al., 2012); setting up of the Lilliput effect that causes organisms to evolve towards becoming smaller and exploit related physiological advantages (Garilli et al., 2015); increasing appearance of harmful marine species (e.g., *Nodularia spumigena* sp., Olli et al., 2015; Jackson, 2008; Paerl and Huisman, 2008) and of toxic compounds (e.g. of the phenolic type, Jin et al., 2015); alteration of fish populations through habitat modification (Nagelkerken et al., 2016), as well as increasing global redistribution of marine biodiversity (Molinos et al., 2016). Finally, such ecological and biogeochemical changes in the oceans could have profound consequences for marine biodiversity, ecosystem-services or processes, and seafood quality with deep implications for fishery industries in the upcoming decades (Doney et al., 2009; Mora et al., 2013; Jin et al., 2015).

7 Perspectives

Ocean acidification is the outcome of a series of anthropic and natural processes that take place at the same time and are often interlinked. The dissolution of increasing atmospheric CO_2 into seawater obviously plays an important role (Pearson and Palmer, 2000; Feely et al., 2008; Beaufort et al., 2011), but there are also important contributions from the degradation of primary producers and DOM (Cai et al., 2011; Sunda and Cai, 2012; Mostofa et al., 2013a). The latter process could be enhanced by an increased oceanic primary productivity (Feng et al., 2009; Sunda and Cai, 2012; Mostofa et al., 2013a), which is one of the possible consequences of global warming (see also supplementary Figure 1) (Feng et al., 2009; Mostofa et al., 2013c). In coastal areas, acid rains and eutrophication caused by the runoff of terrestrial organic matter including DOM and nutrients (Sunda and Cai, 2012; Bauer et al., 2013), combined with microbial and photochemical degradation (Mostofa et al., 2013a), may be important or even the major causes of acidification. All the described processes would increase the supersaturation of the seawater CO_2 that correspondingly reduces the ability of seawater to take up atmospheric CO_2, thereby extending the oceanic areas that constitute a source instead of a sink or carbon dioxide (presently, such areas are mostly concentrated in the equatorial zone) (see Fig. 1). An important issue is that acidification takes place at varying degrees, with different roles of the factors involved and with different impacts depending on the latitude, on the water temperature range as modified by the effects of GW, and on the distance from the coast (Vitousek et al., 1997; Copin-Montégut et al., 2004; Feely et al., 2008; Yamamoto-Kawai et al., 2009; Beaufort et al., 2011; Bates et al., 2013; Kroeker et al., 2013).

Acidification of seawater would be detrimental to marine organisms, and particularly to marine calcifiers for the long-term (*e.g*. homogeneous) acidification of subsurface/deeper seawater and possibly also the short-term (*e.g*. diurnal and abrupt) acidification of upper surface seawater. Therefore, living organisms will have to face multiple stresses at the same time, such as increasing occurrence of reactive oxygen species in the sea surface water, hypoxia in subsurface water, toxic algal blooms and pathogens. Some of these additional stressors and/or their effects could be enhanced by acidification: the oxidative stress tends to be more severe at lower pH values and in the presence of diurnal and abrupt pH variations in surface water; the effects of hypoxia are exacerbated in long-term homogeneously acidified subsurface/deeper seawater, and a decline in marine calcifiers could provide a competitive advantage for toxic algae.

Therefore, ocean acidification is expected to introduce deep changes in marine habitats, and food web processes.

Based on the discussed mechanisms, some of the possible actions that could be taken to limit the future impacts of acidification can be listed here: *(i)* a reduction of anthropic CO_2 emissions to the atmosphere, which should be carried out in the wider context of fighting global warming and will face the same difficulties; *(ii)* the implementation of measures aimed at CO_2 capture, such as a worldwide increase in green plantation. In coastal areas, to limit the effects of acidification, some measures could be taken that are probably of somewhat easier implementation: *(a)* reduction of the inputs to seawater of OM from soil runoff, which implies the control and limitation of land use practices, of soil erosion and of wastewater discharges; *(b)* limitation of the primary productivity by controlling eutrophication, including the release of nutrients from agricultural activities; *(c)* removal of algae (*e.g.* by means of nets) during bloom periods, to avoid fertilization of seawater by the associated nutrients; *(d)* limitation of the emission of pollutants such as nitrogen and sulfur oxides to the atmosphere, as they are precursors of HNO_3 and H_2SO_4 that are involved in acid rains. Finally, marine oceanographers should focus on how marine organisms are affected by short-term pH variations (*e.g*. diurnal and abrupt) in surface waters and by long-term (*e.g*. homogeneous) ones in response to the effects of GW, which may further influence such pH variations.

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Figure Captions

Fig. 1

A conceptual model of acidification in coastal to open oceans, showing either dissolution of atmospheric CO_2 or emission of aquatic CO_2 plus DIC originated from the photoinduced and/or biological respiration of primary producers (PP). The latter includes both dissolved organic matter (DOM) and PP (1). Uptake of such CO_2 is primarily responsible for the occurrence of photosynthesis and PP (2) that can generate algal toxins or pathogens in the euphotic zone, along with generation of CO_2, DIC and other products; PP can also be enhanced by autochthonous DOM (2), by DOM or sinking cells in subsurface or deeper seawater (2), and by riverine DOM (2). Atmospheric acid rain (mostly HNO_3 and H_2SO_4) can contribute directly to the acidification (3). Global warming can lengthen the stratification period with a subsequent decline in vertical mixing, which reduces the exchange with surface oxygenated water (4).

Fig. 2

Diurnal variation of pH along with $f\mathrm{CO}_{2[\mathrm{seawater}]}$ (μatm) and $f\mathrm{CO}_{2[\mathrm{air}]}$ (μatm) in surface seawater of the Jiulongjiang estuary (a) and the Bay of Bengal (b). pH, $f\mathrm{CO}_{2[\mathrm{seawater}]}$ (μatm) and sea subsurface temperature for seawater samples (from 13 to 75 m depth)in the North Yellow Sea (c). Samples from the Jiulongjiang estuary were collected from June 28, 2009 at 16:00 local time (Chinese Standard Time) to June 29, 2009 at 14:55 local time, from 24°25′ to 24°46′N and 118°00′ to 119°19′E. Throughout the sampling period (a) there was a range of salinity (4.4-33.9 psu) and of sea surface water temperature (26.59-29.12 °C). Samples from the Bay of Bengal were collected on May whereas pH, $f\mathrm{CO}_{2[\mathrm{seawater}]}$ and $f\mathrm{CO}_{2[\mathrm{air}]}$ varied from 8.12 to 8.37, 153 to 373 μatm and 370 to 381 μatm, respectively, along with salinity (27.82±0.26 psu), chlorophyll *a* (12.35±2.23 μg L^{-1}), sea surface water temperature (SST: 28.50-31.70 °C) and day-time solar intensity flux (556-109700-17 Lux at 5:00, 12:00 and 18:00 local time, respectively) (b). The calculated pH, salinity, $f\mathrm{CO}_{2[\mathrm{seawater}]}$ at *in situ* DIC and SST varied in the respective ranges 7.53-7.97, 28.24-32 psu, 280-776 μatm and 3.44-20.58 °C for the subsurface samples collected from North Yellow Seawith the range of latitudes is 37°25′-39°67′ N and that of longitudes is 121°16′ -124°10′ E (c).

Fig. 3

Diurnal changes of pH, H_2O_2 and solar (UV) intensity in the seawater of Taira Bay on January 9-10, 2003 (a) and Sesoko Bay on January 19-20, 2003 (b).(c) and (d): pH and concentration of H_2O_2 as a function of the solar UV intensity with the related linear fit regressions in the case of Taira Bay and Sesoko Bay samples, respectively. In the seawater of Taira Bay the pH, H_2O_2, dissolved organic carbon (DOC) and sea surface water temperature (SST) varied in the following ranges: 8.16-8.25, 40-100 nM, 1.14-1.42 ppm, and 18.8-20.9 °C, respectively. In the seawater of Sesoko Bay the relevant ranges were as follows: 7.82-8.28, 30-110 nM, 0.84-1.41 ppm, and 17.7-20.2 °C, respectively.

Fig. 4

Relationship of $PCO_{2[seawater]}$ with pH (a) and dissolved O_2 (b) in subsurface seawater of the Yellow Sea. Decline in dissolved O_2 combined with an increase in dissolved inorganic carbon (DIC), as a function of the incubation time (60 hrs), in an experiment conducted using subsurface seawater from East China Sea (c). Depth ranged from 13 to 75 m for a variety of subsurface seawater samples, with latitudes at 37°25′-39°67′ N and longitudes at 121°16′ -124°10′ E. Ten 60 mL bottles for dissolved O_2 and ten 60 mL borosilicate glass bottles for DIC wrapped with black polyethylene were submerged into an in-flow water bath, in which surface seawater was continuously supplied to control the water bath temperature. Dark incubated samples were collected after 12, 24, and 60 hrs of incubation. Seawater samples for the experiment were collected at 37 m depth on July 2, 2013 using a 10 L Niskin Bottle in East China Sea at 28°50′N, 122°15′E.

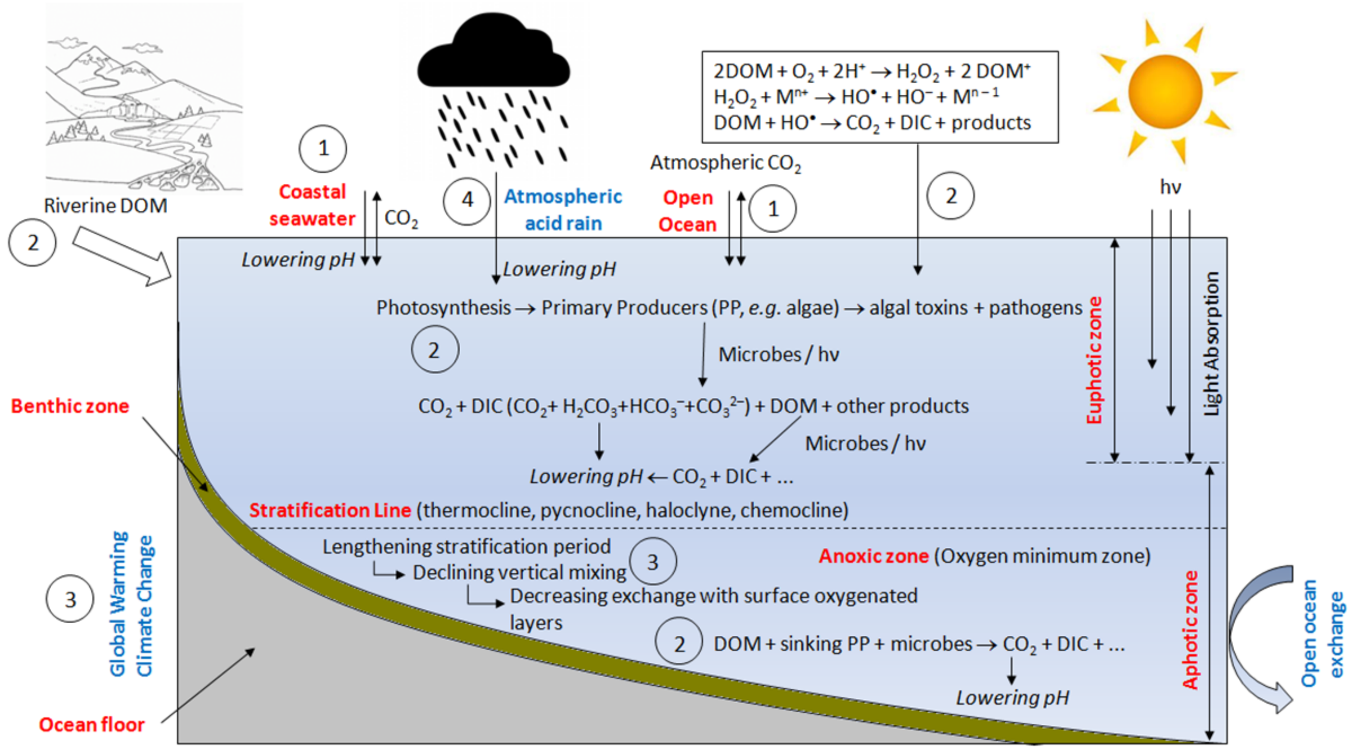
Figure 5

Possible forthcoming changes in pH in the world's oceans. Figure (a) shows the spatial difference between future (i.e., the average from 2091 to 2100) and contemporary (i.e., the average from years 1996 to 2005) values under the RCP85 scenario (decadal averages were chosen to minimize aliasing by interannual variability). Aside each color scale it is provided the absolute change, whereas the numbers on top indicate the rescaled values; complete results for the RCP85 and RCP45 scenarios for the ocean surface and floor are shown in the reference (Mora et al., 2013). Figure (b) shows the global average change relative to contemporary values under the Representative Concentration Pathways 4.5 (RCP45) and 8.5 (RCP85) scenarios at the ocean surface and seafloor; semitransparent lines are the projections for the model.

Fig. 6

An overview of the potential upcoming ecological and biogeochemical consequences, linking different environmental drivers, processes and cycles related to acidification in the future ocean.

Fig. 1



Riverine DOM
Coastal seawater
CO_2
Lowering pH
Atmospheric acid rain
Lowering pH
$2DOM + O_2 + 2H^+ \rightarrow H_2O_2 + 2\,DOM^+$
$H_2O_2 + M^{n+} \rightarrow HO^{\bullet} + HO^- + M^{n-1}$
$DOM + HO^{\bullet} \rightarrow CO_2 + DIC + products$
Atmospheric CO_2
Open Ocean
hν
Photosynthesis → Primary Producers (PP, *e.g.* algae) → algal toxins + pathogens
Microbes / hν
$CO_2 + DIC\ (CO_2 + H_2CO_3 + HCO_3^- + CO_3^{2-})$ + DOM + other products
Microbes / hν
Lowering pH ← CO_2 + DIC + ...
Euphotic zone
Light Absorption
Benthic zone
Stratification Line (thermocline, pycnocline, haloclyne, chemocline)
Lengthening stratification period
Declining vertical mixing
Decreasing exchange with surface oxygenated layers
Anoxic zone (Oxygen minimum zone)
DOM + sinking PP + microbes → CO_2 + DIC + ...
Lowering pH
Aphotic zone
Open ocean exchange
Global Warming
Climate Change
Ocean floor

Fig. 2

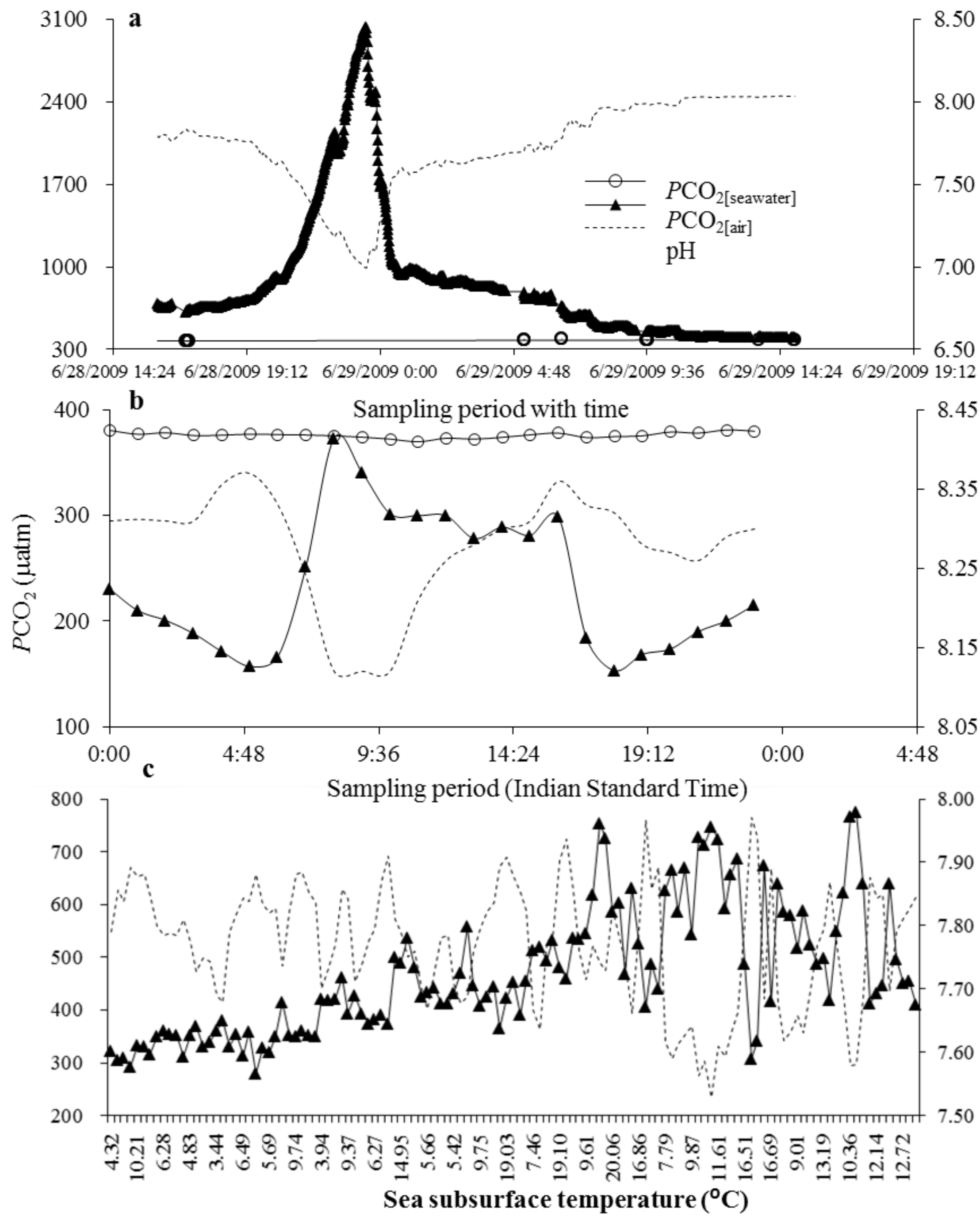

a
3100
2400
1700
1000
300
8.50
8.00
7.50
7.00
6.50
$PCO_{2[seawater]}$
$PCO_{2[air]}$
pH
6/28/2009 14:24
6/28/2009 19:12
6/29/2009 0:00
6/29/2009 4:48
6/29/2009 9:36
6/29/2009 14:24
6/29/2009 19:12
Sampling period with time
b
400
300
200
100
8.45
8.35
8.25
8.15
8.05
PCO_2 (µatm)
pH
0:00
4:48
9:36
14:24
19:12
0:00
4:48
Sampling period (Indian Standard Time)
c
800
700
600
500
400
300
200
8.00
7.90
7.80
7.70
7.60
7.50
4.32
10.21
6.28
4.83
3.44
6.49
5.69
9.74
3.94
9.37
6.27
14.95
5.66
5.42
9.75
19.03
7.46
19.10
9.61
20.06
16.86
7.79
9.87
11.61
16.51
16.69
9.01
13.19
10.36
12.14
12.72
Sea subsurface temperature (°C)

Fig. 3

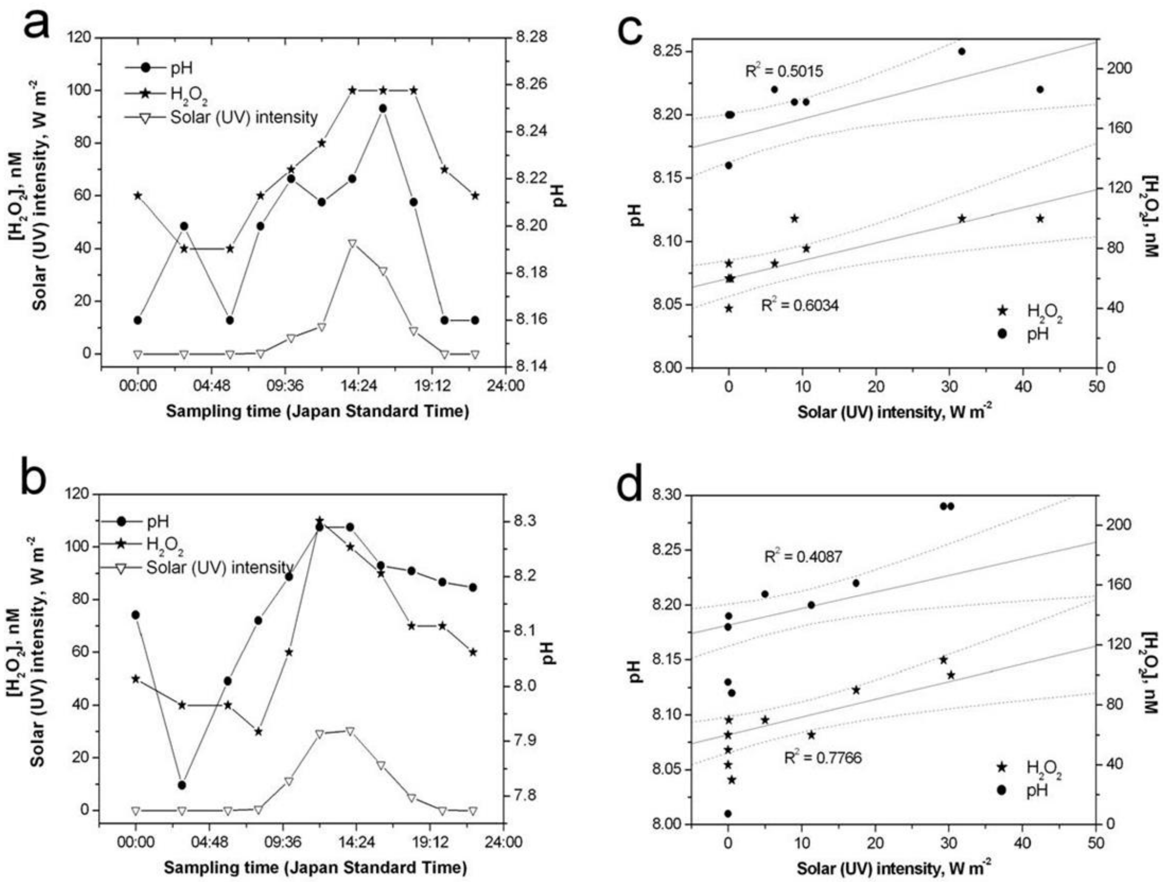

a
pH
H_2O_2
Solar (UV) intensity
$[H_2O_2]$, nM
Solar (UV) intensity, W m^{-2}
pH
Sampling time (Japan Standard Time)
b
pH
H_2O_2
Solar (UV) intensity
$[H_2O_2]$, nM
Solar (UV) intensity, W m^{-2}
pH
Sampling time (Japan Standard Time)
c
R^2 = 0.5015
R^2 = 0.6034
H_2O_2
pH
$[H_2O_2]$, nM
Solar (UV) intensity, W m^{-2}
d
R^2 = 0.4087
R^2 = 0.7766
H_2O_2
pH
$[H_2O_2]$, nM
Solar (UV) intensity, W m^{-2}

Fig. 4

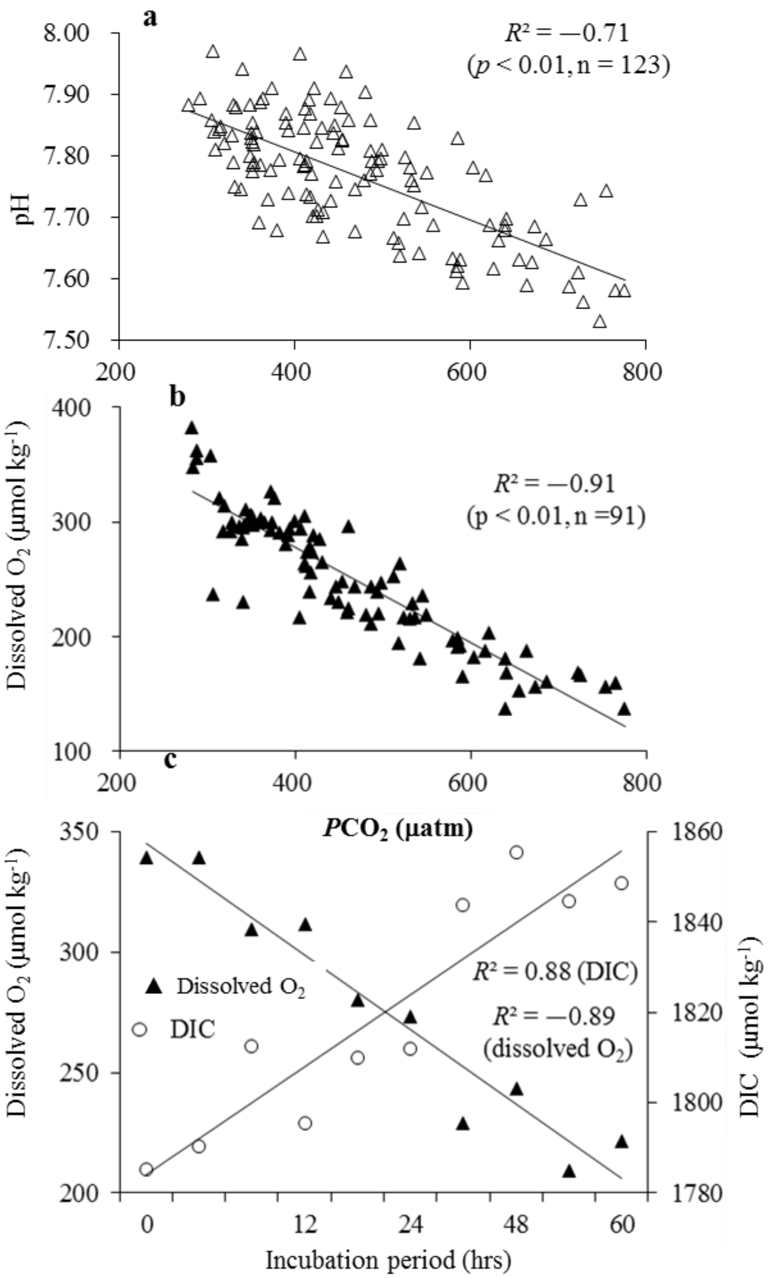

a
R^2 = —0.71
(p < 0.01, n = 123)
pH
8.00
7.90
7.80
7.70
7.60
7.50
200
400
600
800
b
R^2 = —0.91
(p < 0.01, n =91)
Dissolved O_2 (µmol kg^{-1})
400
300
200
100
200
400
600
800
c
$P$$CO_2$ (µatm)
Dissolved O_2 (µmol kg^{-1})
350
300
250
200
Dissolved O_2
DIC
R^2 = 0.88 (DIC)
R^2 = —0.89
(dissolved O_2)
DIC (µmol kg^{-1})
1860
1840
1820
1800
1780
0
12
24
48
60
Incubation period (hrs)

Fig. 5

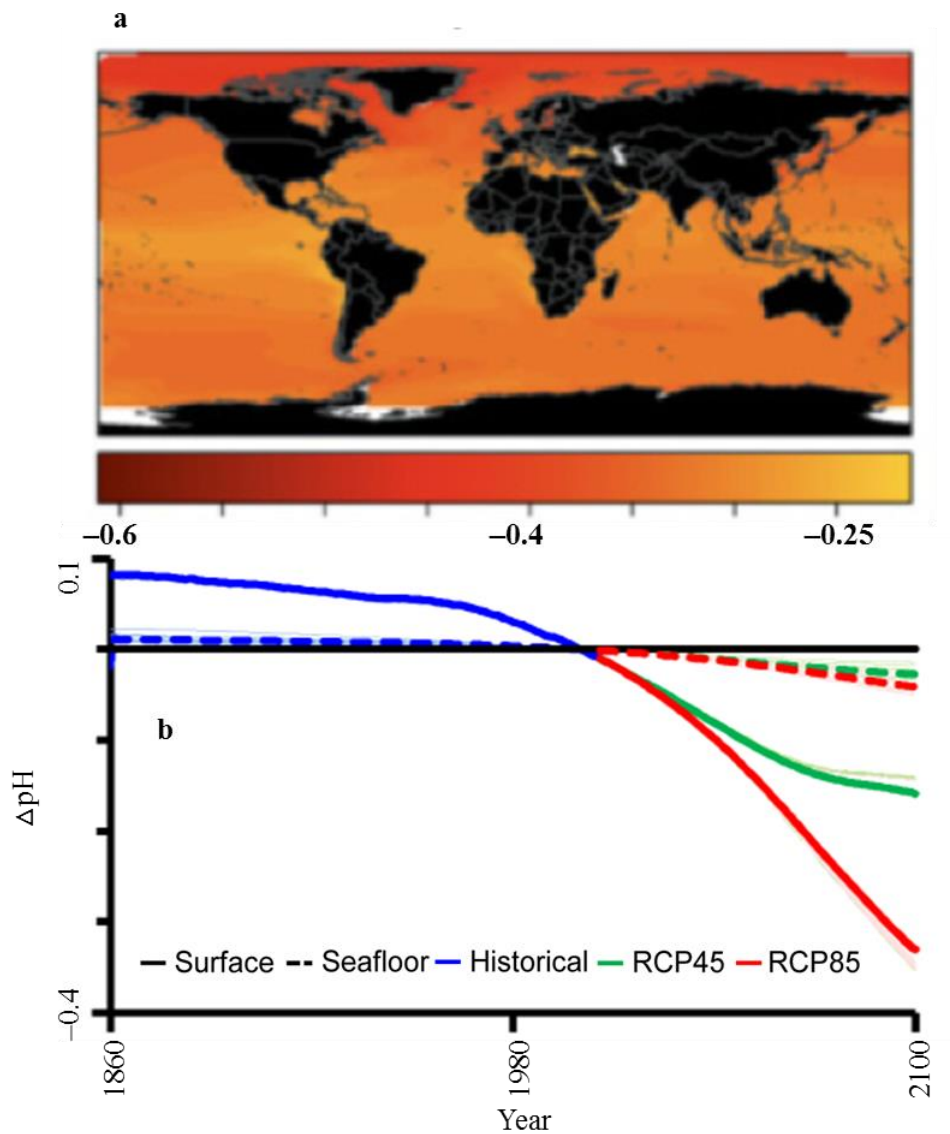
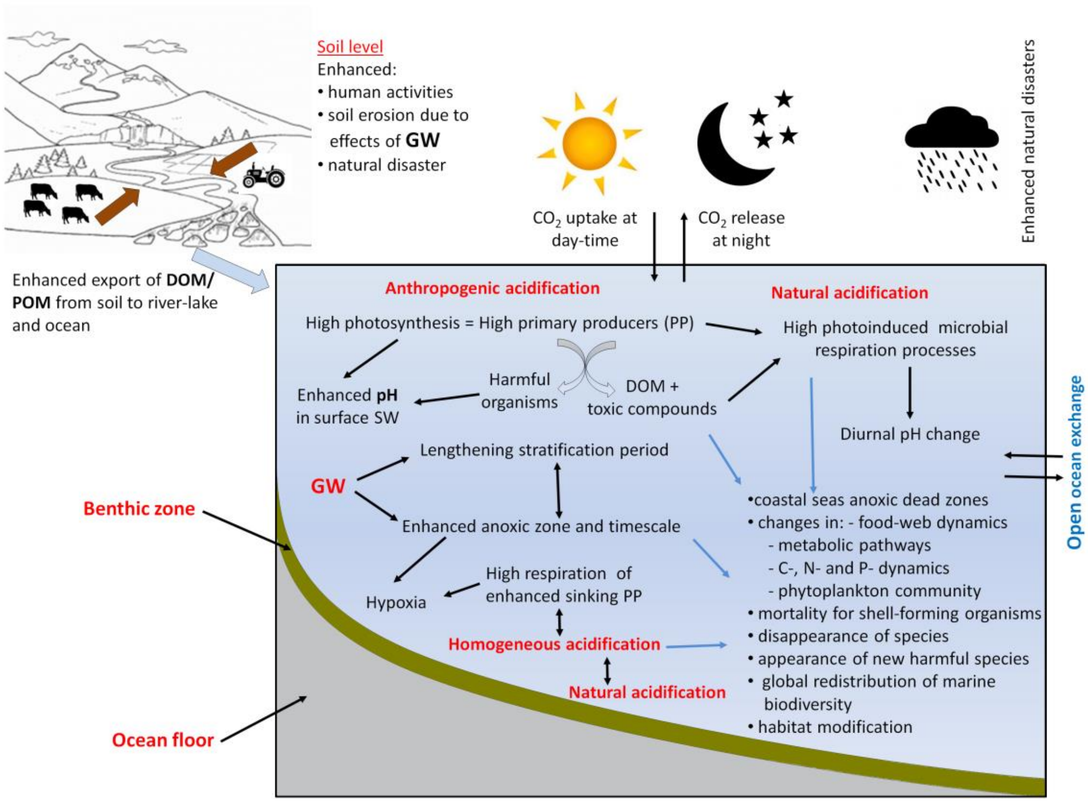

a
−0.6
−0.4
−0.25
0.1
b
ΔpH
−0.4
— Surface -- Seafloor — Historical — RCP45 — RCP85
1860
1980
2100
Year

Fig. 6


Soil level
Enhanced:
• human activities
• soil erosion due to effects of GW
• natural disaster
Enhanced natural disasters
CO_2 uptake at day-time
CO_2 release at night
Enhanced export of DOM/POM from soil to river-lake and ocean
Anthropogenic acidification
Natural acidification
High photosynthesis = High primary producers (PP)
High photoinduced microbial respiration processes
Enhanced pH in surface SW
Harmful organisms
DOM + toxic compounds
Diurnal pH change
Open ocean exchange
Lengthening stratification period
GW
Benthic zone
Enhanced anoxic zone and timescale
•coastal seas anoxic dead zones
• changes in: - food-web dynamics
- metabolic pathways
- C-, N- and P- dynamics
- phytoplankton community
• mortality for shell-forming organisms
• disappearance of species
• appearance of new harmful species
• global redistribution of marine biodiversity
• habitat modification
Hypoxia
High respiration of enhanced sinking PP
Homogeneous acidification
Natural acidification
Ocean floor