Supplement of Biogeosciences, 13, 1767–1786, 2016
http://www.biogeosciences.net/13/1767/2016/
doi:10.5194/bg-13-1767-2016-supplement

Biogeosciences Open Access EGU

Supplement of

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

Khan M. G. Mostofa et al.

Correspondence to: Khan M. G. Mostofa (mostofa@tju.edu.cn) and Cong-Qiang Liu (liucongqiang@vip.skleg.cn)

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

2.1 Increasing dissolution of atmospheric CO_2 to seawater

The exchange of CO_2 between seawater and the atmosphere can take place following different mechanisms and with different features. The outcome is a very varied degree of CO_2 uptake from, and/or emission to, the atmosphere, with time scales for variability that are in the daily to seasonal range. The main situations that may be encountered in seawater are listed below.

2.1.1 Sinking or balance of atmospheric CO_2 to seawater under sunlight, and emission or balance of CO_2 to the atmosphere during the night. This scenario can take place with a time span ranging from minutes to several hours (Biswas et al., 2004; DeGrandpre et al., 1998; Jiang et al., 2011; Nakamura and Nakamori, 2009; Zhang et al., 2013), and two phenomena can be involved: (*i*) Elevated photosynthesis produces a strong consumption of seawater CO_2, thereby decreasing the fugacity of CO_2 (fCO_2) in water and making seawater itself an important sink of atmospheric CO_2. Elevated photosynthesis would be associated to a high degree of degradation/respiration of organic matter includingprimary producers (PP) and dissolved organic matter (DOM), which causes a fast recycling of nutrients and provides optimum conditions for the primary productivity to be high. Such a behavior is generally observed in waters with a high degree of eutrophication. (*ii*) During the night, an elevated degree of degradation/respiration of organic material would substantially increase the fCO_2 in seawater, so that CO_2 will be released to the atmosphere (Ma and Green, 2004; Xie et al., 2004). The high degree of respiration during the night is made possible by the availability of organic material and, produced by the elevated photosynthetic activity at daytime. Highly eutrophic waters with elevated nutrients that show such a behavior can be found in the Jiulongjiang estuary (Fig. 2a), in Mangrove coastal locations (Biswas et al., 2004), in Luhuitou fringing reef, Sanya Bay, South China Sea (Zhang et al., 2013), in the Gulf of Biscay and the North Sea (Frankignoulle and Borges, 2001), in the coastal seawater, Aodi and Nanwan Bay sites, Taiwan (Jiang et al., 2011), in the California coastal waters during the day time (DeGrandpre et al., 1998), in reef crest algal community (Ishigaki Island) Japan (Nakamura and Nakamori, 2009), in reef crest algal community (Ishigaki Island) Japan (Nakamura and Nakamori, 2009), in branching Acropora (coral)

community, Ishigaki Island, Japan (Nakamura and Nakamori, 2009), in montiporastellata (coral) community, Ishigaki Island, Japan (Nakamura and Nakamori, 2009), and in Rukan-sho coral reef, Ishigaki Island, Japan (Ohde and van Woesik, 1999). The inner shelf/coastal waters are more likely to act as sinks of atmospheric CO_2 during daytime (Chen and Borges, 2009; Zhai et al., 2005).

The optimum conditions for such a situation to be found are associated with high primary production and require a sufficient amount of nutrients and light (Behrenfeld et al., 2002). For example, daytime sinking of atmospheric CO_2 can be observed in: in the California coastal waters during the day time (DeGrandpre et al., 1998); in the coastal seawater of the Bay of Bengal in sites (site 3) that are sufficiently rich in nutrients (the same trend is not followed in nutrient-deficient sites) (Akhand et al., 2013), and during the summer period (April-August) in subtropical eutrophic lakes such as Lake Hongfeng and Lake Baihua (Wang et al., 2011). The latter two lakes have both a sufficient amount of nutrients and have high water temperature (*e.g.* 9-26 °C during the whole year), as a consequence of high sunlight intensity (Li et al., 2013; Long et al., 2013).

The balance between the daytime sinking of atmospheric CO_2 and the nighttime emissions to the atmosphere may be variable, depending on the overall conditions and the relative importance of photosynthesis and respiration. For instance, in the equatorial Pacific Ocean it has been shown that the partial pressure of CO_2 (pCO_2) decreased from 430 μatm to 340 μatm while the sea surface temperature increased from 25.4°C to 28.3°C (Goyet and Peltzer, 1997), a possible reason being elevated photosynthesis. In the highly productive Seto Inland Sea, carbon dioxide is released to the atmosphere between June and November, whilst CO_2 uptake by seawater occurs between December and May (Ohtaki et al., 1993).

2.1.2 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. This scenario is typically observed in waters with low photosynthetic activity, where there is limited consumption of CO_2 by photosynthesis during the day and limited degradation/respiration of organic matter in the night time (Fransson et al., 2004; Kuffner et al., 2008; Yates et al., 2007; Zhai et al., 2005). Such conditions are typically observed in waters that are characterized by a low level of nutrients or sunlight irradiation, and/or in the presence of temporary factors such as sunlight limitation because of cloudy weather or precipitation. The fluxes of CO_2 between the atmosphere and seawater could depend for instance on the water temperature, as more elevated daytime temperature would decrease the solubility of CO_2 in water and the reverse would happen during the night. The daytime emission of CO_2 from seawater would also be favored by the respiration/degradation of organic matter. Such a scenario is often observed in waters where the primary production is limited by the availability of nutrients, even in the presence of relatively elevated

amounts of organic carbon. These conditions can be found in the Jiulongjiang estuary (Fig. 2a), in the Tampa and Florida Bay (Yates et al., 2007); in the northern South China Sea (Dai et al., 2009), in the salt marshes and mangroves (Chen and Borges, 2009), in the outer shelf/open ocean (Chen and Borges, 2009; Zhai et al., 2005) and in the Coral reef (mesocosm), Moku O Loe, Kaneohe Bay, Hawaii (Kuffner et al., 2008). The availability of nutrients, with typically seasonal time scales, influences photosynthesis under conditions of elevated illumination in the surface layer (light saturation). In contrast, in deeper waters photosynthesis responds on a shorter time scale to variations of incoming irradiance, light attenuation and mixing layer depth (Behrenfeld et al., 2002).

2.1.3 Emission or balance of seawater CO_2 to the atmosphere during both day and night. This scenario (Borges and Frankignoulle, 2003; Goyet and Peltzer, 1997; Kayanne et al., 2005; Nakamura and Nakamori, 2009) is observed when CO_2 is produced by degradation/respiration of organic matter (and also by abiotic photodegradation in daytime), and when photosynthesis is unable to uptake the generated carbon dioxide. The consequence is an increase of seawater fCO_2 and a subsequent release of the excess CO_2 to the atmosphere. Typical reasons for this scenario may be lack or scarcity of nutrients and/or light, the latter because of *e.g.* cloudy weather. Such water characteristics may be found in the Bay of Seine (Borges and Frankignoulle, 2003), in inner estuaries and near-shore coastal areas, or in low-latitude shelves (Chen and Borges, 2009), in the coastal seawater (site 3) of the Bay of Bengal (Akhand et al., 2013), in the equatorial Pacific Ocean that linked to day-time increase in temperature (Goyet and Peltzer, 1997), mostly source in the Southern Ocean surface water at sites WIE and APF2 (Fransson et al., 2004), in coral reef in Ishigaki Island, Japan in summer (Kayanne et al., 2005), and in *pocilloporaverrucosa-tabular*Acropora (coral) community, Ishigaki Island, Japan (Nakamura and Nakamori, 2009).

2.1.4 Sinking or balance of atmospheric CO_2 to surface water during both day and night. The main difference between this scenario and scenario #2 is that, in the present case, daytime photosynthesis occurs to a higher extent and it is able to deplete seawater CO_2, thereby causing a net uptake of carbon dioxide by seawater. Moreover, the organic material generated during the day is not degraded to a sufficient extent in nighttime to make the seawater fCO_2 increase above the atmospheric level. As in the case of scenario #2, such conditions can be observed in water where the primary production is limited by nutrients and/or light. These characteristics can be found in open shelves in temperate and high-latitude regions, during all seasons (Chen and Borges, 2009), in the Belgian coastal seawater (Borges and Frankignoulle, 1999), in surface waters of the Galician upwelling system (Borges and Frankignoulle, 2001), mostly sinking in the Southern Ocean surface water at site SIE1 (Fransson et al., 2004), in the surface seawater (east of Gotland) in the

Baltic Sea (Wesslander et al., 2011), and mostly sinking in coral reef in Ishigaki Island, Japan in winter (Kayanne et al., 2005).

2.1.5 Sinking or source or balance of atmospheric CO_2 to surface water during the warm period. This scenario generally takes place in highly productive and nutrient-rich waters (Arrigo et al., 2008; Borges and Frankignoulle, 1999; Thomas et al., 2005; Zhai and Dai, 2009; Zhai et al., 2005). During summer CO_2 is consumed by the elevated photosynthesis, which takes place under optimum conditions as far as both nutrients and light are concerned (Arrigo et al., 2008). Degradation/respiration of organic matter does not keep pace with photosynthesis, and the decrease of seawater fCO_2 causes a net uptake of carbon dioxide from the atmosphere. During the winter season, the reduction of solar intensity and the shorter day-time ensure that respiration/degradation prevail over photosynthesis, thereby increasing the fCO_2 in water at levels comparable to or above those of the atmosphere. Under such circumstances, emission of carbon dioxide by seawater can be observed. Wintertime emission of CO_2 to the atmosphere is generally found in the South China Sea (Zhai et al., 2009; Zhai et al., 2005; Zhai et al., 2013), in the East China Sea (Shim et al., 2007; Zhai and Dai, 2009), in the Bay of Bengal (Biswas et al., 2004), in coral reef in Ishigaki Island, Japan (Kayanne et al., 2005), in a few sampling sites in North Sea (Thomas et al., 2004), in the Southern Bight of the North Sea (Schiettecatte et al., 2007), in the English Channel and adjacent seawater (Borges and Frankignoulle, 2003), in the Scheldt plume off the Belgian coast (Borges and Frankignoulle, 2002), in the seawater of Northwestern Mediterranean Sea (Copin-Montégut et al., 2004), in the mid and outer shelf of US Middle Atlantic Bight (DeGrandpre et al., 2002), in the coastal upwelling system (Gago et al., 2003), mostly sinking in the Gulf of Biscay (Frankignoulle and Borges, 2001), mostly source in the Kaneohe Bay, Oahu, Hawaii (Fagan and Mackenzie, 2007), mostly sinking in the seawater of the Gotland Sea (Kuss et al., 2004; Schneider et al., 2003), mostly sinking in the Chukchi Sea adjacent to the Arctic Ocean (Bates, 2006), mostly source in the Antarctic shelf waters of Southern Ocean (Arrigo et al., 2008), mostly source in the seawater of the Bermuda coral reef system (Bates, 2002), mostly sinking in the Chukchi Sea adjacent to the Arctic Ocean along 65–75°N and 150–170°W (Bates, 2006), in the Southern Ocean (Arrigo et al., 2008), in the Ross Sea (Sweeney, 2003), and strong sinking during the summer period than in winter in the Gulf of Biscay (Frankignoulle and Borges, 2001).

2.1.6 Emission or sinking or balance of seawater CO_2 to the atmosphere during cold period. This scenario is similar to scenario #5 and takes place in the similar types of seawaters (Bates, 2006; Borges and Frankignoulle, 2003; Thomas et al., 2004). Such a scenario is observed in a few sampling sites of North Sea (Thomas et al., 2004), in the

Southern Bight of the North Sea (Schiettecatte et al., 2007), in the English Channel and adjacent seawater (Borges and Frankignoulle, 2003), in the South China Sea (Zhai et al., 2013), in the coastal seawater in the Bay of Bengal (Biswas et al., 2004) (Biswaste al., 2004), in the seawater of Northwestern Mediterranean Sea (Copin-Montégut et al., 2004), in the mid and outer shelf of US Middle Atlantic Bight (DeGrandpre et al., 2002), mostly source in the seawater of the Gotland Sea (Kuss et al., 2004; Schiettecatte et al., 2007), mostly source in the Scheldt plume off the Belgian coast (Borges and Frankignoulle, 2002), mostly source in the upper reach of the Pearl River Estuary near South China Sea (Dai et al., 2006), in the Kaneohe Bay, Oahu, Hawaii (Fagan and Mackenzie, 2007), mostly sinking in the Antarctic shelf waters of Southern Ocean (Arrigo et al., 2008), mostly sinking in the seawater of the Bermuda coral reef system (Bates, 2002), mostly sinking in the Chukchi Sea adjacent to the Arctic Ocean along 65–75^{O}N and 150–170^{O}W (Bates, 2006), mostly sinking in East China Sea (Zhai and Dai, 2009), mostly sinking in the Atlantic sector, the Southern Ocean (Chierici et al., 2004), and mostly sinking in coral reef in Ishigaki Island, Japan (Kayanne et al., 2005).

Overall, the subtropical-tropical marginal seas and the continental shelves at low latitudes and the equatorial Pacific (14°N–14°S) act as sources of CO_2 to the atmosphere whilst the marginal seas and continental shelves at mid-high latitudes and the temperate oceans between141 and 501 in the both hemispheres acts as a strong sink of atmospheric CO_2 (Borges, 2005; Borges et al., 2005; Cai et al., 2006; Chen and Borges, 2009; Takahashi et al., 2009). Correspondingly, coral reefs act either as a sourceof $CO_2$to the atmosphere(Bates, 2002; Gattuso et al., 1999; Ware et al., 1992) or a oceanic sink (Bates, 2002; Gattuso et al., 1997; Kraines et al., 1996). But such conclusions might not be precisely true in a variety of seawater that sampled once during the day time at the same location. Six different scenarios of CO_2 in seawaters configured that seawater can act as a source or sink or balance of CO_2 to the atmosphere which also significantly varied with seasons affecting many factors (see the main text). This therefore indicates that the diurnal variation of CO_2 is very important for better understanding of the ocean acidification as well as CO_2 behavior in the world's oceans, and this issue should be the focus for further study.

2.3 Enhanced PP and respiration due to the effects of global warming and other processes (Some remaining contents of this section)

The enhancement of photosynthesis and primary production depends on several factors, and those which prevail are linked to the nutrient status of water. Photosynthesis is usually favored by enhanced input of terrestrial DOM into water (Bauer et al., 2013; Porcal et al., 2009), but in DOM-rich waters the regeneration of autochthonous DOM and nutrients from PP plays a more important role. In the presence of sufficient light or high WT under GW conditions, such factors can also lead to harmful algal blooms (Fig. S1)

(Mostofa et al., 2013a). A link between DOM or PP and algal blooms or eutrophication may be observed when the regeneration of nutrients (NH_4^+, NO_3^- and NO_2^-) is operational (Cai et al., 2011; Mostofa et al., 2013a). In contrast, transformation of nitrogen-containing nutrients to N_2 (Doney et al., 2007; Kuypers et al., 2003; Ward, 2013) largely eliminates the connection (Mostofa et al., 2013a).

The primary production and the occurrence of DOM in seawater are linked to several other processes, including: *(i)* the increase in atmospheric CO_2 (Feng et al., 2009; Gruber et al., 2002; Hein and Sand-Jensen, 1997; Le Quéré et al., 2009; Schippers et al., 2004); *(ii)* the increased input of terrestrial OM and nutrients, because of human-induced alteration of land use (Cai et al., 2006; Smith et al., 1999; Vitousek et al., 1997) and because of enhanced soil erosion rates due to extreme climate weathering (Nearing et al., 2004); *(iii)* the input of organic contaminants and nutrients from anthropogenic activities (*e.g*. sewerage, industries, pharmaceuticals, or intensive fish cage farming (Fu et al., 2010; Mostofa et al., 2013a; Nyenje et al., 2010; Pergent‐Martini et al., 2006) ; *(iv)* large ecological changes in forests (Graven et al., 2013) and transportation of OM by weathering, combined with high terrestrial plant productivity induced by increasing atmospheric CO_2 (Regnier et al., 2013); *(v)* atmospheric acid rain/precipitation (notably HNO_3 and H_2SO_4) (Baker et al., 2007; Teira et al., 2013) and *(vi)* the effects of GW (Fig. S1) (Engel et al., 2012; Feng et al., 2009; Hein and Sand-Jensen, 1997; Mostofa et al., 2013b; Schippers et al., 2004). Many of the described phenomena are mostly susceptible to affect coastal waters which, by the way, host between15% and30% of the oceanic primary production and80% of the OM burial (Gattuso et al., 1998). Coastal waters also account for most of the benthic oceanic $CaCO_3$ production, for 20% of the surface pelagic $CaCO_3$ stock (Balch et al., 2005), and for50% of the oceanic $CaCO_3$ deposition (Gattuso et al., 1998).

Some of the above-mentioned factors which affect primary production in seawater are also closely interlinked. For instance, the increase of atmospheric temperature due to GW could enhance DOM leaching from terrestrial soils because of high soil respiration, and the DOM contents in surface waters could increase as a consequence (Porcal et al., 2009). Increased atmospheric CO_2 would also increase the turnover rates of soil OM, driven by the enhanced activity of soil microorganisms (Blagodatskaya et al., 2010) and including a higher rate of decomposition of older and fresh plant residues (Blagodatskaya et al., 2010; Dorodnikov M, 2011). Note that elevated CO_2 was shown to enhance soil OM mineralization by 83–218% in a simulated wetland (Wolf et al., 2007). A net increase of C emissions to the atmosphere would thus be induced by enhanced respiration of soil OM under global warming condition (Davidson and Janssens, 2006; Knorr et al., 2005).

The increase of net primary production in seawater is responsible for the gradual increase of CO_2 in the surface seawater of some oceans, including the ice-free Arctic Ocean Basin

(Cai et al., 2010), the area near the Canary Islands (ESTOC), located in the northeast Atlantic subtropical gyre (González-Dávila et al., 2003), and in the Northern Hemisphere (Graven et al., 2013). Enrichment of surface seawater in CO_2 means that oceanic water behaves less effectively as a sink and could even become a net CO_2 source to the atmosphere, as is presently the case for the equatorial Pacific (Takahashi et al., 2009). Average rates of increase in surface-water fCO_2 have been quantified, on the basis of deseasonalized data, as 1.5 µatm y^{-1}. The basin- specific rates varied between 1.2±0.5 and 2.1±0.4 µatm y^{-1} over the North Atlantic, North and South Pacific and Southern Oceans, which cover about 27% of the global ocean areas (Takahashi et al., 2002; Takahashi et al., 2009). Furthermore, the role of low-latitude continental shelves as net sources of CO_2 to the atmosphere is thought to be a consequence of both GW that increases WT and to higher inputs of terrestrial organic carbon (Cai et al., 2006; Corbière et al., 2007). The effect of GW on the release of CO_2 to the atmosphere is related to a series of processes, including lower solubility of CO_2 in warmer waters, increased stratification and the effects on primary productivity (Keeling, 2005). Coastal waters are also more susceptible to acidification than the open ocean, because of the effects of eutrophication (such as emission of CO_2 by respiration and mineralization of organic N and P) that decreases the buffering capacity of seawater. The combination of increasing atmospheric CO_2 and of processes occurring in seawater produces different critical scenarios, which are observed for CO_2 emissions from seabed and for sinking of anthropic atmospheric CO_2 to seawater (see also supplementary section) (Borges and Gypens, 2010; Cai et al., 2011; Dore et al., 2009). Moreover, changes in the biogenic carbon flow in response to sea surface warming have the potential to reduce the transfer of primary produced OM to higher trophic levels (Laws et al., 2000; Vázquez-Domínguez et al., 2007; Wohlers et al., 2009). Such processes would weaken the ocean's biological carbon pump and would provide a positive feedback to the rise of atmospheric CO_2 (Laws et al., 2000; Vázquez-Domínguez et al., 2007; Wohlers et al., 2009).

2.3.1 Impacts of nitrification-denitrification and sulfate reduction on acidification

Nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ or $NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2\ H^+ + H_2O$) (Doney et al., 2007) caused by ammonia-oxidizing bacteria, such as *Nitrosomonas* and *Nitrobacter* (Martens-Habbena et al., 2009) can contribute to acidification, and it is for instance partially responsible for the acidification of coastal seawater (Doney et al., 2007). Denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$), caused by denitrifying bacteria (Pan et al., 2013) is an important process that occurs in oxygen minimum zones (OMZs) and accounts for approximately 71% of the nitrogen loss, while anaerobic ammonium oxidation (anammox) accounts for the remaining 29% (Ward, 2013). An important issue is that increasing atmospheric CO_2 is expected to significantly modify the occurrence of microorganisms in oceanic water and to favor global N_2 fixation and

possibly denitrification, probably at the expense of nitrification (Hutchins et al., 2013). Denitrification stimulates the acidification by producing an effective total alkalinity flux in seawater (Chen and Wang, 1999; Thomas et al., 2009). However, in addition to the processes already shown, one should consider that ammonium and nitrate also take part to additional cycles. It has been shown that NO_3^-–supported PP generates alkalinity (106 CO_2 + 16 NO_3^- + 138 H_2O → organics + 16 OH^- + 138 O_2), but the resulting basification would only partially compensate for acidification if nitrate is generated by the oxidation of ammonium according to the reaction $2NH_3 + 4O_2 \rightarrow 2NO_3^- + 2H_2O + 2H^+$; note that ammonium oxidation to nitrate yields 2 H^+ per processed NH_4^+, while incorporation of nitrate into organic nitrogen only consumes one H^+ per nitrate ion processed. On the contrary, NH_4^+–supported PP eliminates alkalinity according to the overall reaction: 106 CO_2 + 16 NH_4^+ + 106 H_2O → organics + 16 H^+ + 106 O_2 (Doney et al., 2007). On the other hand, anaerobic ammonium oxidation ($NH_4^+ + NO_2^- \rightarrow N_2H_4 \rightarrow N_2$) carried out by anammox bacteria (Ward, 2013) is H^+-neutral ($NH_4^+ + NO_2^- \rightarrow N_2 + 2\ H_2O$).

In addition to potentially affecting the pH of seawater, the nitrogen cycle processes are also substantially influenced by pH itself. For instance, nitrification rates decrease to zero at a pH around 6.0–6.5, where the NH_3 substrate is practically all protonated to ammonium (Huesemann et al., 2002). In fact, the proportions of NH_3 to NH_4^+ and of PO_4^{3-} to HPO_4^{2-} are both very sensitive to small pH variations around 8.0 according to the following equations

$$\frac{[NH_3]}{[NH_4^+]} = \frac{k_a}{[H^+]} \qquad \text{eq. 1}$$

$$\frac{[PO_4^{-3}]}{[HPO_4^{-2}]} = \frac{k_{a1}\, k_{a2}\, k_{a3}}{[H^+]\, k_{a1}\, k_{a2}} \qquad \text{eq. 2}$$

note that pK_a for NH_4^+ is 9.3 and the three pK_as for H_3PO_4 are 2.2, 7.1 and 12,4, respectively(Zeebe and Wolf-Gladrow, 2001). Moreover, the nitrogen cycle may be closely interlinked with that of carbon. For instance, the anaerobic oxidation of CH_4 to CO_2 is connected either to the reduction of NO_3^- to NO_2^- and then N_2, or to anammox that yields N_2 as well (Haroon et al., 2013). The conversion of SO_4^{2-} into H_2S, carried out by sulfate-reducing bacteria such as desulfobacterales, desulfovibrionales and syntrophobacterales (Muyzer and Stams, 2008) which can either be emitted to the atmosphere or be buried as pyrite, also significantly increases the total alkalinity (Chen and Wang, 1999). Therefore, denitrification and SO_4^{2-} reduction can raise the buffering capacity of CO_2 that stimulates the acidification of seawater (Chen and Wang, 1999; Thomas et al., 2009). Note that each mole of denitrified N and reduced SO_4^{2-}reduction can release 0.99 and 1.98 mol of total alkalinity, respectively (Chen and Wang, 1999).

2.4 **Direct acidification and stimulation of PP by atmospheric acid rain:** Natural and anthropogenic ocean acidification

Atmospheric acid rain can decrease the pH of seawater directly, by the input of HNO_3 and H_2SO_4, and indirectly through the addition of NH_4^+ (Bates and Peters, 2007; Doney et al., 2007). In fact, most of the anthropogenic NH_3 and NH_4^+ (~ 98%) are nitrified to nitrate in the upper ocean releasing H^+ ions ($NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$; see also the previous section). This issue causes the effective net atmospheric input of ammonium to be acidic (Doney et al., 2007). A rough estimate shows that direct atmospheric acidic depositions could contribute 2% to the acidification of surface waters in the subtropical North Atlantic Ocean since the early 1980's (Bates and Peters, 2007).

Another important impact of rainfall in general, including the acidic one is the stimulating effect on primary production, as shown by field observations and experimental simulations (Baker et al., 2007; Paerl and Fogel, 1994; Teira et al., 2013). As discussed earlier, the enhanced primary production can contribute to seawater acidification through increased CO_2. Note that atmospheric rainfall can bring nutrients to seawater, including NO_3^-, NH_4^+ and PO_4^{3-} (Doney et al., 2007; Paerl and Fogel, 1994), Fe^{2+} and Fe^{3+} (Baker et al., 2007; Kieber et al., 2001), dissolved Si (Baker et al., 2007) and other major ions such as F^-, Cl^-, SO_4^{2-}, K^+, Na^+, Ca^{2+}, Mg^{2+}, Co^{2+} and Zn^{2+} (Baker et al., 2007; Zhang et al., 2007). Other compounds contained in rainwater that could stimulate photosynthesis under definite conditions are H_2O_2, aldehydes and organic acids (Sakugawa et al., 1993), as well as other dissolved organic substances (Kieber et al., 2006). *In situ* incubation experiments demonstrate that chlorophyll *a* concentration is increased by 2.6 times with the addition of 10% (v/v) rainwater (Zou et al., 2000). Microcosm experiments on the effect of rainwater addition to natural marine plankton populations also showed an increase in bacterial abundance and production (Teira et al., 2013). Another issue is that rainfall on land can produce an important input of OM and nutrients in seawater *via* terrestrial runoff. In addition to the possible stimulation of acidification processes, the direct or indirect (though runoff) fertilization of seawater carried out by rain could contribute to the occurrence of harmful algal blooms and to the generation of pathogens (Doney et al., 2007; Flewelling et al., 2005; Sekar et al., 2006; Sunda and Cai, 2012; Teira et al., 2013).

References

Akane, S., Makino, S., Hashimoto, N., Yatsuzuka, Y., Kawai Yu, T. K., and Sakugawa, H.: Hydrogen peroxide in the sea water of Hiroshima Bay Japan. Oceanogr. Jpn., 13, 185-196, 2004.

Akhand, A., Chanda, A., Dutta, S., Manna, S., Sanyal, P., Hazra, S., Rao, K., and Dadhwal, V.: Dual character of Sundarban estuary as a source and sink of CO_2 during summer: an investigation of spatial dynamics. Environ. Monit. Assess., 185, 6505-6515, 2013.

Arakaki, T., Fujimura, H., Hamdun, A.M., Okada, K., Kondo, H., Oomori, T., Tanahara, A., and Taira, H.: Simultaneous measurement of hydrogen peroxide and Fe species: (Fe(II) and Fe(tot)) in Okinawa Island Seawater: impacts of red soil pollution. J. Oceanogr., 61, 561-568, 2005.

Arrigo, K. R., van Dijken, G., and Long, M.: Coastal Southern Ocean: A strong anthropogenic CO_2 sink. Geophys. Res. Lett., 35, L21602, 2008.

Avery Jr, G. B., Cooper, W. J., Kieber, R. J., and Willey, J. D.: Hydrogen peroxide at the Bermuda Atlantic Time Series Station: Temporal variability of seawater hydrogen peroxide. Mar. Chem., 97, 236-244, 2005.

Baker, A. R., Weston, K., Kelly, S. D., Voss, M., Streu, P., and Cape, J. N.: Dry and wet deposition of nutrients from the tropical Atlantic atmosphere: Links to primary productivity and nitrogen fixation. Deep Sea Res. Part I, 54, 1704-1720, 2007.

Balch, W., Gordon, H. R., Bowler, B., Drapeau, D., and Booth, E.: Calcium carbonate measurements in the surface global ocean based on Moderate-Resolution Imaging Spectroradiometer data. J. Geophys. Res., 110, C(7), 2005.

Bates, N. R.: Seasonal variability of the effect of coral reefs on seawater CO2 and air-sea CO2 exchange. Limnol. Oceanogr., 47, 43-52, 2002.

Bates, N. R.: Air-sea CO_2 fluxes and the continental shelf pump of carbon in the Chukchi Sea adjacent to the Arctic Ocean. J. Geophys. Res., 111, C10013, 2006.

Bates, N. R., and Peters, A. J.: The contribution of atmospheric acid deposition to ocean acidification in the subtropical North Atlantic Ocean. Mar. Chem., 107, 547-558, 2007.

Bauer, J. E., and Cai, W.-J., Raymond, P.A., Bianchi, T. S., Hopkinson, C. S., Regnier, P. A.: The changing carbon cycle of the coastal ocean. Nature, 504, 61-70, 2013.

Behrenfeld, M. J., Marañón, E., Siegel, D. A., and Hooker, S. B.: Photoacclimation and nutrient-based model of light-saturated photosynthesis for quantifying oceanic primary production. Mar. Ecol. Prog. Ser., 228, 103-117, 2002.

Biswas, H., Mukhopadhyay, S., De, T., Sen, S., and Jana, T.: Biogenic controls on the air-water carbon dioxide exchange in the Sundarban mangrove environment, northeast coast of Bay of Bengal, India. Limnol. Oceanogr., 49, 95-101, 2004.

Blagodatskaya, E., Blagodatsky, S., Dorodnikov, M., and Kuzyakov, Y.: Elevated atmospheric CO_2 increases microbial growth rates in soil: results of three CO2 enrichment experiments. Glob. Change Biol., 16, 836-848, 2010.

Booth, J. A. T., McPhee-Shaw, E. E., Chua, P., Kingsley, E., Denny, M., Phillips, R., Bograd, S. J., Zeidberg, L. D., and Gilly, W. F.: Natural intrusions of hypoxic, low pH water into nearshore marine environments on the California coast. Cont. Shelf Res., 45, 108-115, 2012.

Borges, A.: Do we have enough pieces of the jigsaw to integrate CO_2 fluxes in the coastal ocean? Estuaries, 28, 3-27, 2005.

391 Borges, A., and Frankignoulle, M.:1999) Daily and seasonal variations of the partial pressure of CO_2 in
392 surface seawater along Belgian and southern Dutch coastal areas. J. Mar. Syst., 19, 251-266, 1999.
393 Borges, A., and Gypens, N.: Carbonate chemistry in the coastal zone responds more strongly to
394 eutrophication than to ocean acidification. Limnol. Oceanogr., 55, 346-353, 2010.
395 Borges, A. V., Delille, B., and Frankignoulle, M.: Budgeting sinks and sources of CO_2 in the coastal ocean:
396 Diversity of ecosystems counts. Geophys. Res. Lett., 32, L14601, 2005.
397 Borges, A. V., and Frankignoulle, M.: Short-term variations of the partial pressure of CO_2 in surface waters
398 of the Galician upwelling system. Prog. Oceanogr., 51, 283-302, 2001.
399 Borges, A. V., and Frankignoulle, M.: Distribution and air-water exchange of carbon dioxide in the Scheldt
400 plume off the Belgian coast. Biogeochemistry, 59, 41-67, 2002.
401 Borges, A. V., and Frankignoulle, M.: Distribution of surface carbon dioxide and air-sea exchange in the
402 English Channel and adjacent areas. J. Geophys. Res., 108, 3140, 2003.
403 Byrne, R. H., Mecking, S., Feely, R. A., and Liu, X.: Direct observations of basin-wide acidification of the
404 North Pacific Ocean. Geophys. Res. Lett., 37, L02601, 2010.
405 Cai, W.-J., Chen, L., Chen, B., Gao, Z., Lee, S.H., Chen, J., Pierrot, D., Sullivan, K., Wang, Y., Hu, X.,
406 Huang, W.-J., Zhang, Y., Xu, S., Murata, A., Grebmeier, J. M., Jones, E. P., and Zhang, H.: Decrease
407 in the CO_2 uptake capacity in an ice-free Arctic Ocean basin. Science 329, 556-559, 2010.
408 Cai, W. J., Dai, M., and Wang, Y.: Air-sea exchange of carbon dioxide in ocean margins: A province-based
409 synthesis. Geophys. Res. Lett. 33, 2006.
410 Cai, W. J., Hu, X., Huang, W. J., Murrell, M. C., Lehrter, J. C., Lohrenz, S. E., Chou, W. C., Zhai, W.,
411 Hollibaugh, J. T., and Wang, Y.: Acidification of subsurface coastal waters enhanced by
412 eutrophication. Nature Geosci., 4, 766-770, 2011.
413 Chen, C.-T. A., and Borges, A. V.: Reconciling opposing views on carbon cycling in the coastal ocean:
414 Continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO_2. Deep Sea Res.
415 Part II, 56, 578-590, 2009.
416 Chen, C. T. A., and Wang, S. L.: Carbon, alkalinity and nutrient budgets on the East China Sea continental
417 shelf. J. Geophys. Res., 104, 20675-20686, 1999.
418 Chierici, M., Fransson, A., Turner, D. R., Pakhomov, E. A., and Froneman, P. W.: Variability in pH, fCO2,
419 oxygen and flux of CO2 in the surface water along a transect in the Atlantic sector of the Southern
420 Ocean. Deep Sea Res. Part II, 51, 2773-2787, 2004.
421 Clark, C. D., De Bruyn, W. J., Hirsch, C. M., and Jakubowski, S. D.: Hydrogen peroxide measurements in
422 recreational marine bathing waters in Southern California, USA. Water Res. 44, 2203-2210, 2010.
423 Copin-Montégut, C., Bégovic, M., and Merlivat, L.: Variability of the partial pressure of CO_2 on diel to
424 annual time scales in the Northwestern Mediterranean Sea. Mar. Chem., 85, 169-189, 2004.
425 Corbière, A., Metzl, N., Reverdin, G., Brunet, C., and Takahashi, T.: Interannual and decadal variability of
426 the oceanic carbon sink in the North Atlantic subpolar gyre. Tellus B, 59, 168-178, 2007.
427 Cyronak, T., Santos, I. R., McMahon, A., and Eyre, B. D.: Carbon cycling hysteresis in permeable
428 carbonate sands over a diel cycle: Implications for ocean acidification. Limnol. Oceanogr., 58, 131-
429 143, 2013.
430 Dai, M., Guo, X., Zhai, W., Yuan, L., Wang, B., Wang, L., Cai, P., Tang, T., and Cai, W.-J.: Oxygen
431 depletion in the upper reach of the Pearl River estuary during a winter drought. Mar. Chem., 102, 159-
432 169, 2006.
433 Dai, M., Lu, Z., Zhai, W., Chen, B., Cao, Z., Zhou, K., Cai, W.-J., and Chen, C.-T. A.: Diurnal variations
434 of surface seawater pCO:2) in contrasting coastal environments. Limnol. Oceanogr., 54, 735–745,
435 2009.
436 Dai, M., Zhai, W., Cai, W.-J., Callahan, J., Huang, B., Shang, S., Huang, T., Li, X., Lu, Z., and Chen, W.:
437 Effects of an estuarine plume-associated bloom on the carbonate system in the lower reaches of the
438 Pearl River estuary and the coastal zone of the northern South China Sea. Cont. Shelf Res., 28, 1416-
439 1423, 2008.
440 Davidson, E. A., and Janssens, I. A.: Temperature sensitivity of soil carbon decomposition and feedbacks
441 to climate change. Nature, 440, 165-173, 2006.
442 DeGrandpre, M., Hammar, T., and Wirick, C.: Short-term pCO_2 and O_2 dynamics in California coastal
443 waters. Deep-Sea Res. Part II, 45, 1557-1575, 1998.
444 DeGrandpre, M., Olbu, G., Beatty, C., and Hammar, T.: Air–sea CO_2 fluxes on the US Middle Atlantic
445 Bight. Deep Sea Res. Part II, 49, 4355-4367, 2002.

Delille, B., Delille, D., Fiala, M., Prevost, C., and Frankignoulle, M.: Seasonal changes of pCO_2 over a subantarctic Macrocystis kelp bed. Polar Biol., 23, 706-716, 2000.

Doney, S. C., Mahowald, N., Lima, I., Feely, R. A., Mackenzie, F. T., Lamarque, J. F., and Rasch, P. J.: Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. Proc. Nat. Aca. Sci., 104, 14580-14585, 2007.

Dore, J. E., Lukas, R., Sadler, D. W., Church, M. J., and Karl, D. M.: Physical and biogeochemical modulation of ocean acidification in the central North Pacific. Proc. Nat. Aca. Sci., 106, 12235-12240, 2009.

Dorodnikov M, K.Y., Fangmeier A, and Wiesenberg G. L. B.: C and N in soil organic matter density fractions under elevated atmospheric CO2: turnover vs stabilization. Soil Biol. Biochem., 43, 579–589, 2011.

Engel, A., Borchard, C., Piontek, J., Schulz, K. G., Riebesell, U., and Bellerby, R.: CO_2 increases ^{14}C-primary production in an Arctic plankton community. Biogeosciences, 9, 1290-1308, doi:10.5194/bg-10-1291-2013, 2013.

Fagan, K. E., and Mackenzie, F. T.: Air–sea CO_2 exchange in a subtropical estuarine-coral reef system, Kaneohe Bay, Oahu, Hawaii. Mar. Chem., 106, 174-191, 2007.

Feely, R. A., Alin, S. R., Newton, J., Sabine, C.L., Warner, M., Devol, A., Krembs, C., and Maloy, C.: The combined effects of ocean acidification, mixing, and respiration on pH and carbonate saturation in an urbanized estuary. Estuar. Coast. Shelf Sci., 88, 442-449, 2010.

Feng, Y., Hare, C. E., Leblanc, K., Rose, J. M., Zhang, Y., DiTullio, G. R., Lee, P., Wilhelm, S., Rowe, J. M., and Sun, J.: The Effects of Increased pCO_2 and Temperature on the North Atlantic Spring Bloom: I. The Phytoplankton Community and Biogeochemical Response. Mar. Ecol. Prog. Ser., 388, 13-25, 2009.

Findlay, H. S., Hennige, S. J., Wicks, L. C., Navas, J. M., Woodward, E. M. S., and Roberts, J. M.: Fine-scale nutrient and carbonate system dynamics around cold-water coral reefs in the northeast Atlantic. Sci. Rep., 4, 3671, 2014.

Flewelling, L. J., Naar, J. P., Abbott, J. P., Baden, D. G., Barros, N. B., Bossart, G. D., Bottein, M.-Y. D., Hammond, D. G., Haubold, E. M., and Heil, C. A.: Brevetoxicosis: Red tides and marine mammal mortalities. Nature, 435, 755-756, 2005.

Frankignoulle, M., and Borges, A. V.: European continental shelf as a significant sink for atmospheric carbon dioxide. Glob. Biogeochem. Cyc., 15, 569-576, 2001.

Frankignoulle, M., Bourge, I., Canon, C., and Dauby, P.: Distribution of surface seawater partial C02 pressure in the English Channel and in the Southern Bight of the North Sea. Cont. Shelf Res., 16, 381-395, 1996.

Fransson, A., Chierici, M., and Anderson, L. G.: Diurnal variability in the oceanic carbon dioxide system and oxygen in the Southern Ocean surface water. Deep Sea Res. Part II, 51, 2827-2839, 2004.

Fu, P., Mostofa, K. M. G., Wu, F., Liu, C.-Q., Li, W., Liao, H., Wang, L., Wang, J., and Mei, Y.: Excitation-emission matrix characterization of dissolved organic matter sources in two eutrophic lakes:Southwestern China Plateau). Geochem. J., 44, 99, 2010.

Gagliano, M., McCormick, M. I., Moore, J. A., and Depczynski, M.: The basics of acidification: baseline variability of pH on Australian coral reefs. Mar. Biol., 157, 1849-1856, 2010.

Gago, J., Gilcoto, M., Pérez, F. F., and Rıos, A.: Short-term variability off CO_2 in seawater and air–sea CO_2 fluxes in a coastal upwelling system (Ría de Vigo, NW Spain). Mar. Chem., 80, 247-264, 2003.

Gattuso, J.-P., Frankignoulle, M., and Smith, S. V.: Measurement of community metabolism and significance in the coral reef CO_2 source-sink debate. Proc. Nat. Aca. Sci., 96, 13017-13022, 1999.

Gattuso, J.-P., Frankignoulle, M., and Wollast, R.: Carbon and carbonate metabolism in coastal aquatic ecosystems. Ann. Rev. Ecol. Syst., 29, 405-434, 1998.

Gattuso, J. P., Payri, C. E., Pichon, M., Delesalle, B., and Frankignoulle, M.: Primary production, calcification, and air-sea CO_2 fluxes of a macroalgal-dominated coral reef community:Moorea, French Polynesia). J. Phycol., 33, 729-738, 1997.

González-Dávila, M., Santana-Casiano, J. M., Rueda, M.-J., Llinás, O., and González-Dávila, E.-F.: Seasonal and interannual variability of sea-surface carbon dioxide species at the European Station for Time Series in the Ocean at the Canary Islands:ESTOC) between 1996 and 2000. Glob. Biogeochem. Cyc., 17, 1076, 2003.

Goyet, C., and Peltzer, E. T.: Variation of CO_2 partial pressure in surface seawater in the equatorial Pacific Ocean. Deep Sea Res. Part I, 44, 1611-1625, 1997.

Graven, H. D., Keeling, R. F., Piper, S. C., Patra, P. K., Stephens, B. B., Wofsy, S. C., Welp, L. R., Sweeney, C., Tans, P. P., Kelley, J. J., Daube, B. C., Kort, E. A., Santoni, G. W., and Bent, J. D.: Enhanced seasonal exchange of CO_2 by northern ecosystems since 1960. Science, 341: 1085-1089, 2013.

Gruber, N., Keeling, C. D., and Bates, N. R.: Interannual variability in the North Atlantic Ocean carbon sink. Science, 298, 2374-2378, 2002.

Hall-Spencer, J. M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S. M., Rowley, S. J., Tedesco, D., and Buia, M.-C.: Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. Nature, 454, 96-99, 2008.

Haroon, M. F., Hu, S., Shi, Y., Imelfort, M., Keller, J., Hugenholtz, P., Yuan, Z., and Tyson, G. W.: Anaerobic oxidation of methane coupled to nitrate reduction in a novel archaeal lineage. Nature, 500, 567–570, 2013.

Hein, M., and Sand-Jensen, K.: CO_2 increases oceanic primary production. Nature, 388, 526-527, 1997.

Herut, B., Shoham-Frider, E., Kress, N., Fiedler, U., and Angel, D. L.: Hydrogen peroxide production rates in clean and polluted coastal marine waters of the Mediterranean, Red and Baltic Seas. Mar. Pollut. Bull., 36, 994-1003, 1998.

Hofmann, G. E., Smith, J. E., Johnson, K. S., Send, U., Levin, L. A., Micheli, F., Paytan, A., Price, N. N., Peterson, B., and Takeshita, Y.: High-frequency dynamics of ocean pH: a multi-ecosystem comparison. PloS one 6, e28983, 2011.

Huesemann, M. H., Skillman, A. D., and Crecelius, E. A.: The inhibition of marine nitrification by ocean disposal of carbon dioxide. Mar. Pollut. Bull., 44, 142-148, 2002.

Hutchins, D. A., Fu, F.-X., Webb, E. A., Walworth, N., and Tagliabue, A.:2013) Taxon-specific response of marine nitrogen fixers to elevated carbon dioxide concentrations. Nature Geosci., 6, 790-795, 2013.

Invers, O., Romero, J., and Pérez, M.: Effects of pH on seagrass photosynthesis: a laboratory and field assessment. Aquat. Bot., 59, 185-194, 1997.

Jiang, Z.-P., Huang, J.-C., Dai, M., Kao, S. J., Hydes, D. J., Chou, W.-C., and Jan, S.: Short-term dynamics of oxygen and carbon in productive nearshore shallow seawater systems off Taiwan: Observations and modeling. Limnol. Oceanogr., 56, 1832-1849, 2011.

Kayanne, H., Hata, H., Kudo, S., Yamano, H., Watanabe, A., Ikeda, Y., Nozaki, K., Kato, K., Negishi, A., and Saito, H.: Seasonal and bleaching-induced changes in coral reef metabolism and CO_2 flux. Glob. Biogeochem. Cyc., 19, GB3015, 2005.

Keeling, R. F.: Comment on "The Ocean sink for anthropogenic CO_2". Science 308, 1743c, 2005.

Kieber, R. J., Whitehead, R. F., Reid, S. N., Willey, J. D., and Seaton, P. J.: Chromophoric dissolved organic matter (CDOM) in rainwater, southeastern North Carolina, USA. J. Atmos. Chem., 54, 21-41, 2006.

Kieber, R. J., Williams, K., Willey, J. D., Skrabal, S., and Avery Jr, G. B.: Iron speciation in coastal rainwater: concentration and deposition to seawater. Mar. Chem., 73, 83-95, 2001.

Knorr, W., Prentice, I. C., House, J. I., and Holland, E. A.: Long-term sensitivity of soil carbon turnover to warming. Nature, 433, 298-301, 2005.

Kraines, S., Suzuki, Y., Yamada, K., and Komiyama, H.: Separating biological and physical changes in dissolved oxygen concentration in a coral reef. Limnol. Oceanogr., 41, 1790-1799, 1996.

Kuffner, I. B., Andersson, A. J., Jokiel, P. L., Rodgers, K. U. S., and Mackenzie, F. T.: Decreased abundance of crustose coralline algae due to ocean acidification. Nature Geosci. 1, 114-117, 2008.

Kuss, J., Nagel, K., and Schneider, B.: Evidence from the Baltic Sea for an enhanced CO_2 air–sea transfer velocity. Tellus B, 56, 175-182, 2004.

Kuypers, M. M. M., Sliekers, A. O., Lavik, G., Schmid, M., Jorgensen, B. B., Kuenen, J. G., Sinninghe Damste, J. S., Strous, M., and Jetten, M. S. M.: Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. Nature, 422, 608-611, 2003.

Laws, E. A., Falkowski, P. G., Smith, W. O., Ducklow, H., and McCarthy, J. J.: Temperature effects on export production in the open ocean. Glob. Biogeochem. Cyc., 14, 1231-1246, 2000.

Le Quéré, C., Raupach, M. R., Canadell, J. G., and Marland, G.: Trends in the sources and sinks of carbon dioxide. Nature Geosci., 2, 831-836, 2009.

Li, Q., Chen, L., Chen, F., Gao, T., Li, X., Liu, S., and Li, C.: Maixi River estuary to the Baihua Reservoir in the Maotiao River catchment: phytoplankton community and environmental factors. Chin. J. Oceanol. Limnol., 31, 290-299, 2013.

Long, S.-X., Chen, C., Liu, Z.-W., and Ye, X.-Y.: Relationship between phytoplankton and environment factors in Lake Hongfeng. J. Environ. Biol., 34, 445-449, 2013.
Ma, X., and Green, S. A.: Photochemical transformation of dissolved organic carbon in Lake Superior—An in-situ experiment. J. Great Lakes Res., 30, 97-112, 2004.
Manzello, D. P.: Ocean acidification hot spots: Spatiotemporal dynamics of the seawater CO_2 system of eastern Pacific coral reefs. Limnol. Oceanogr., 55, 239-248, 2010.
Martens-Habbena, W., Berube, P. M., Urakawa, H., de la Torre, J.R., and Stahl, D. A.: Ammonia oxidation kinetics determine niche separation of nitrifying Archaea and Bacteria. Nature, 461, 976-979, 2009.
Matson, P. G., Martz, T. R., and Hofmann, G. E.: High-frequency observations of pH under Antarctic sea ice in the southern Ross Sea. Antarct. Sci.,23, 607-613, 2011.
Menéndez, M., Martínez, M., and Comín, F. A.: A comparative study of the effect of pH and inorganic carbon resources on the photosynthesis of three floating macroalgae species of a Mediterranean coastal lagoon. J. Exp. Mar. Biol. Ecol., 256, 123-136, 2001.
Middelboe, A. L., and Hansen, P. J.: High pH in shallow-water macroalgal habitats. Mar. Ecol. Prog. Ser., 338, 107-117, 2007.
Mostofa, K. M. G., Liu, C.-Q., Vione, D., Gao, K., and Ogawa, H.: Sources, factors, mechanisms and possible solutions to pollutants in marine ecosystems. Environ. Pollut., 182, 461-478, 2013a.
Mostofa, K. M. G., Liu, C.-Q., Gao, K., Li, S., Vione, D., and Mottaleb, M. A.: Impacts of Global Warming on Biogeochemical Cycles in Natural Waters, in: Photobiogeochemistry of Organic Matter: Principles and Practices in Water Environments, edited by: Mostofa, K. M. G., Yoshioka, T., Mottaleb, M. A., and Vione, D., Springer, Berlin Heidelberg, 851-914, 2013b.
Muyzer, G., and Stams, A. J.: The ecology and biotechnology of sulphate-reducing bacteria. Nature Rev. Microbiol., 6, 441-454, 2008.
Nakamura, T., and Nakamori, T.: Estimation of photosynthesis and calcification rates at a fringing reef by accounting for diurnal variations and the zonation of coral reef communities on reef flat and slope: a case study for the Shiraho reef, Ishigaki Island, southwest Japan. Coral Reefs, 28, 229-250, 2009.
Nearing, M., Pruski, F., and O'neal, M.:2004) Expected climate change impacts on soil erosion rates: a review. J. Soil Water Conservat., 59, 43-50, 2004.
Nyenje, P., Foppen, J., Uhlenbrook, S., Kulabako, R., and Muwanga, A.: Eutrophication and nutrient release in urban areas of sub-Saharan Africa—a review. Sci. Total Environ., 408, 447-455, 2010.
Ohde, S., and van Woesik, R.: Carbon dioxide flux and metabolic processes of a coral reef, Okinawa. Bull. Mar. Sci., 65, 559-576, 1999.
Ohtaki, E., Yamashita, E., and Fujiwara, F.: Carbon dioxide in surface seawaters of the Seto Inland Sea, Japan. J. Oceanogr., 49, 295-303, 1993.
Paerl, H., and Fogel, M.: Isotopic characterization of atmospheric nitrogen inputs as sources of enhanced primary production in coastal Atlantic Ocean waters. Mar. Biol., 119, 635-645, 1994.
Pan, Y., Ni, B.-J., and Yuan, Z.: Modeling Electron Competition among Nitrogen Oxides Reduction and N2O Accumulation in Denitrification. Environ. Sci. Technol., 47, 11083-11091, 2013.
Pergent-Martini, C., Boudouresque, C. F., Pasqualini, V., and Pergent, G.: Impact of fish farming facilities on Posidonia oceanica meadows: A review. Mar. Ecol., 27, 310-319, 2006.
Porcal, P., Koprivnjak, J.-F., Molot, L. A., and Dillon, P. J.: Humic substances—part 7: the biogeochemistry of dissolved organic carbon and its interactions with climate change. Environ. Sci. Pollut. Res., 16, 714-726, 2009.
Price, N. N., Martz, T. R., Brainard, R. E., and Smith, J. E.: Diel variability in seawater pH relates to calcification and benthic community structure on coral reefs. PloS one 7, e43843, 2012.
Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, I. A., Laruelle, G. G., Lauerwald, R., Luyssaert, S., and Andersson, A. J.: Anthropogenic perturbation of the carbon fluxes from land to ocean. Nature Geosci. 6, 597-607, 2013
Sakugawa, H., Kaplan, I. R., and Shepard, L. S.: Measurements of H_2O_2, aldehydes and organic acids in Los Angeles rainwater: Their sources and deposition rates. Atmos. Environ., 27, 203-219, 1993.
Sakugawa, H., Takami, A., Kawai, H., Takeda, K., Fujiwara, K., and Hirata, S.: The Occurrence of Organic Peroxides in Seawater, in: Dynamics and characterization of marine organic matter, edited by: Handa, N., Tanoue, E., and Hama, T., Springer, Tokyo, 231-240, 2000.
Sakugawa H., Yamashita, T., and Fujiwara K.:1995) Global Fluxes of Carbon and Its Related Substances in the Coastal Sea-ocean-atmosphere System: Proceedings of the 1994 Sapporo IGBP Symposium, 14-17 November 1994, Hokkaido University, Sapporo Hokkaido, Japan. M & J International.

Santos, I. R., Glud, R. N., Maher, D., Erler, D., and Eyre, B. D.: Diel coral reef acidification driven by porewater advection in permeable carbonate sands, Heron Island, Great Barrier Reef. Geophys. Res. Lett., 38, L03604, 2011.

Schiettecatte, L.-S., Thomas, H., Bozec, Y., and Borges, A.: High temporal coverage of carbon dioxide measurements in the Southern Bight of the North Sea. Mar. Chem., 106, 161-173, 2007.

Schippers, P., Lürling, M., and Scheffer, M.: Increase of atmospheric CO_2 promotes phytoplankton productivity. Ecol. Lett., 7, 446-451, 2004.

Schneider, B., Nausch, G., Nagel, K., and Wasmund, N.: The surface water CO_2 budget for the Baltic Proper: a new way to determine nitrogen fixation. J. Mar. Syst., 42, 53-64, 2003.

Sekar, R., Mills, D. K., Remily, E. R., Voss, J. D., and Richardson, L. L.: Microbial communities in the surface mucopolysaccharide layer and the black band microbial mat of black band-diseased Siderastrea siderea. Appl. Environ. Microbial., 72, 5963-5973, 2006.

Semesi, I. S., Beer, S., and Björk, M.: Seagrass photosynthesis controls rates of calcification and photosynthesis of calcareous macroalgae in a tropical seagrass meadow. Mar. Ecol. Prog. Ser., 382, 41-47, 2009.

Shim, J., Kim, D., Kang, Y. C., Lee, J.H., Jang, S.-T., and Kim, C.-H.: Seasonal variations in pCO_2 and its controlling factors in surface seawater of the northern East China Sea. Cont. Shelf Res., 27, 2623-2636, 2007.

Smith, V. H., Tilman, G. D., and Nekola, J. C.: Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environ. Pollut., 100, 179-196, 1999.

Sunda, W.G., and Cai, W.-J.: Eutrophication induced CO_2-acidification of subsurface coastal waters: Interactive effects of temperature, salinity, and atmospheric PCO_2. Environ. Sci. Technol., 46, 10651-10659, 2012.

Suzuki, A., and Kawahata, H.: Partial pressure of carbon dioxide in coral reef lagoon waters: comparative study of atolls and barrier reefs in the Indo-Pacific Oceans. J. Oceanogr., 55, 731-745, 1999.

Sweeney, C.: The annual cycle of surface water CO_2 and O_2 in the Ross Sea: A model for gas exchange on the continental shelves of Antarctica. Antarct. Res. Ser., 78, 295-312, 2003.

Taguchi, F., and Fujiwara, T.: Carbon dioxide stored and acidified low oxygen bottom waters in coastal seas, Japan. Estuar. Coast. Shelf Sci., 86, 429-433, 2010.

Takahashi, T., Sutherland, S. C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N., Wanninkhof, R., Feely, R.A., and Sabine, C.: Global sea–air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects. Deep Sea Res. Part II, 49, 1601-1622, 2002.

Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., Hales, B., Friederich, G., Chavez, F., and Sabine, C.: Climatological mean and decadal change in surface ocean pCO_2, and net sea–air CO_2 flux over the global oceans. Deep Sea Res. Part II, 56, 554-577, 2009.

Teira, E., Hernando-Morales, V., Martínez-García, S., Figueiras, F. G., Arbones, B., and Álvarez-Salgado, X. A.: Response of bacterial community structure and function to experimental rainwater additions in a coastal eutrophic embayment. Estuar. Coast. Shelf Sci., 119, 44-53, 2013.

Thomas, H., Bozec, Y., Elkalay, K., De Baar, H., Borges, A., and Schiettecatte, L.-S.: Controls of the surface water partial pressure of CO_2 in the North Sea. Biogeosciences 2, 323-334, 1726-4189/bg/2005-2-323, 2005.

Thomas, H., Bozec, Y., Elkalay, K., and de Baar, H. J. W.: Enhanced open ocean storage of CO_2 from shelf sea pumping. Science, 304, 1005-1008, 2004.

Thomas, H., Schiettecatte, L.-S., Suykens, K., Koné, Y., Shadwick, E., Prowe, A., Bozec, Y., de Baar, H. J., and Borges, A.: Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments. Biogeosciences, 6, 267–274, doi:10.5194/bg-6-267-2009, 2009.

Vázquez-Domínguez, E., Vaqué, D., and Gasol, J. M.: Ocean warming enhances respiration and carbon demand of coastal microbial plankton. Glob. Change Biol., 13, 1327-1334, 2007.

Vitousek, P. M., Aber, J. D., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., Schlesinger, W. H., and Tilman, D. G.: Human alteration of the global nitrogen cycle: sources and consequences. Ecol. Appl., 7, 737-750, 1997.

Wang, F., Wang, B., Liu, C.-Q., Wang, Y., Guan, J., Liu, X., and Yu, Y.: Carbon dioxide emission from surface water in cascade reservoirs–river system on the Maotiao River, southwest of China. Atmos. Environ., 45, 3827-3834, 2011.

Wang, S.-L., Arthur Chen, C.-T., Hong, G.-H., and Chung, C.-S.: Carbon dioxide and related parameters in the East China Sea. Cont. Shelf Res., 20, 525-544, 2000.

669 Ward, B.B.: How Nitrogen Is Lost. Science, 341, 352-353, 2013.
670 Ware, J. R., Smith, S. V., and Reaka-Kudla, M. L.: Coral reefs: sources or sinks of atmospheric CO_2? Coral
671 Reefs, 11, 127-130, 1992.
672 Wesslander, K., Hall, P., Hjalmarsson, S., Lefevre, D., Omstedt, A., Rutgersson, A., Sahlée, E., and
673 Tengberg, A.: Observed carbon dioxide and oxygen dynamics in a Baltic Sea coastal region. J. Mar.
674 Syst., 86, 1-9, 2011.
675 Wohlers, J., Engel, A., Zöllner, E., Breithaupt, P., Jürgens, K., Hoppe, H.-G., Sommer, U., and Riebesell,
676 U.: Changes in biogenic carbon flow in response to sea surface warming. Proc. Nat. Aca. Sci., 106,
677 7067-7072, 2009.
678 Wolf, A. A., Drake, B. G., Erickson, J. E., and Megonigal, J. P.: An oxygen-mediated positive feedback
679 between elevated carbon dioxide and soil organic matter decomposition in a simulated anaerobic
680 wetland. Glob. Change Biol., 13, 2036-2044, 2007.
681 Xie, H., Zafiriou, O. C., Cai, W.-J., Zepp, R. G., and Wang, Y.: Photooxidation and its effects on the
682 carboxyl content of dissolved organic matter in two coastal rivers in the southeastern United States.
683 Environ. Sci. Technol., 38, 4113-4119, 2004.
684 Yates, K. K., Dufore, C., Smiley, N., Jackson, C., and Halley, R. B.: Diurnal variation of oxygen and
685 carbonate system parameters in Tampa Bay and Florida Bay. Mar. Chem., 104, 110-124, 2007.
686 Yuan, J., and Shiller, A. M.: The distribution of hydrogen peroxide in the southern and central Atlantic
687 ocean. Deep Sea Res. Part II, 48, 2947-2970, 2001.
688 Zeebe, R. E., and Wolf-Gladrow, D.: CO_2 in seawater: Equilibrium, kinetics, isotopes. Elsevier, 2001.
689 Zhai, W. D., and Dai, M.: On the seasonal variation of air–sea CO_2 fluxes in the outer Changjiang:Yangtze
690 River) Estuary, East China Sea. Mar. Chem., 117, 2-10, 2009.
691 Zhai, W. D., Dai, M., and Cai, W.-J.: Coupling of surface pCO_2 and dissolved oxygen in the northern South
692 China Sea: impacts of contrasting coastal processes. Biogeosciences, 6, 2589–2598, doi:10.5194/bg-6-
693 2589-2009, 2009.
694 Zhai, W. D., Dai, M., Cai, W.-J., Wang, Y., and Hong, H.: The partial pressure of carbon dioxide and air–
695 sea fluxes in the northern South China Sea in spring, summer and autumn. Mar. Chem., 96, 87-97,
696 2005.
697 Zhai, W. D., Dai, M., and Guo, X.: Carbonate system and CO_2 degassing fluxes in the inner estuary of
698 Changjiang:Yangtze) River, China. Mar. Chem., 107, 342-356, 2007.
699 Zhai, W., Zhao, H., Zheng, N., and Xu, Y.: Coastal acidification in summer bottom oxygen-depleted waters
700 in northwestern-northern Bohai Sea from June to August in 2011. Chin. Sci. Bull. 57, 1062-1068,
701 2012.
702 Zhai, W. D., Dai, M. H., Chen, B. S., Guo, X. H., Li, Q., Shang, S. L., Zhang, C.Y ., Cai, W. J., and Wang,
703 D. X.: Seasonal variations of air-sea CO_2 fluxes in the largest tropical marginal sea (South China Sea)
704 based on multiple-year underway measurements. Biogeosciences 10, 7775–7791, doi:10.5194/bg-10-
705 7775-2013, 2013.
706 Zhai, W. D., Zheng, N., Huo, C., Xu, Y., Zhao, H. D., Li, Y. W., Zang, K. P., Wang, J. Y., and Xu, X. M.:
707 Subsurface pH and carbonate saturation state of aragonite on the Chinese side of the North Yellow
708 Sea: seasonal variations and controls. Biogeosciences, 11, 1103-1123, doi:10.5194/bg-11-1103-2014,
709 2014.
710 Zhang, C., Huang, H., Ye, C., Huang, L., Li, X., Lian, J., and Liu, S.: Diurnal and seasonal variations of
711 carbonate system parameters on Luhuitou fringing reef, Sanya Bay, Hainan Island, South China Sea.
712 Deep Sea Res. Part II, 96, 65-74, 2013.
713 Zhang, M., Wang, S., Wu, F., Yuan, X., and Zhang, Y.: Chemical compositions of wet precipitation and
714 anthropogenic influences at a developing urban site in southeastern China. Atmos. Res., 84, 311-322,
715 2007.
716 Zou, L., Chen, H. T., and Zhang, J.: Experimental examination of the effects of atmospheric wet deposition
717 on primary production in the Yellow Sea. J. Exp. Mar. Biol. Ecol., 249, 111-121, 2000.
718
719
720

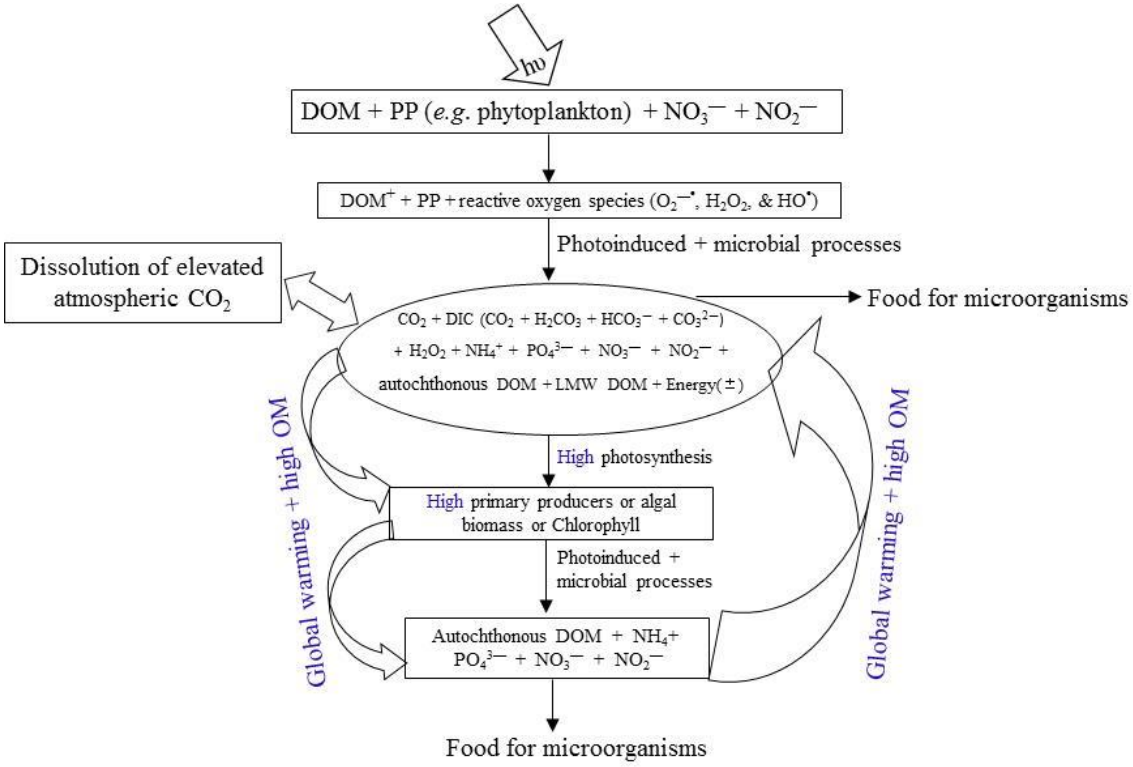

Figure S1. A conceptual schematic diagram about the response to global warming effects and high organic matter (OM) including DOM and PP, as well as the possible effects on the occurrence of harmful algal blooms in water. First, photoinduced transformation is the primary step for the generation of the oxidizing species (*e.g.* H_2O_2 and $HO^{\bullet}$) from DOM. Such processes, along with biological ones, can drive respiration/degradation of DOM and dead organisms, yielding a variety of intermediates and byproducts among which CO_2, DIC, and nutrients (NO_3^-, PO_4^{3-}). Second, such products can enhance photosynthesis with a subsequent increase of the PP (phytoplankton). Third, PP further induces photoinduced and microbial respiration that releases autochthonous DOM and nutrients. Fourth, autochthonous DOM and nutrients undergo photoinduced and microbial degradation that further yields CO_2, DIC and again nutrients. Increased temperature following global warming and input of high OM in water can favor the occurrence of high photosynthesis for a longer period of time and, as a consequence, enhance primary production. This issue can lead to an increase of the worldwide incidence of harmful algal blooms, in waters with high contents of DOM and PP.

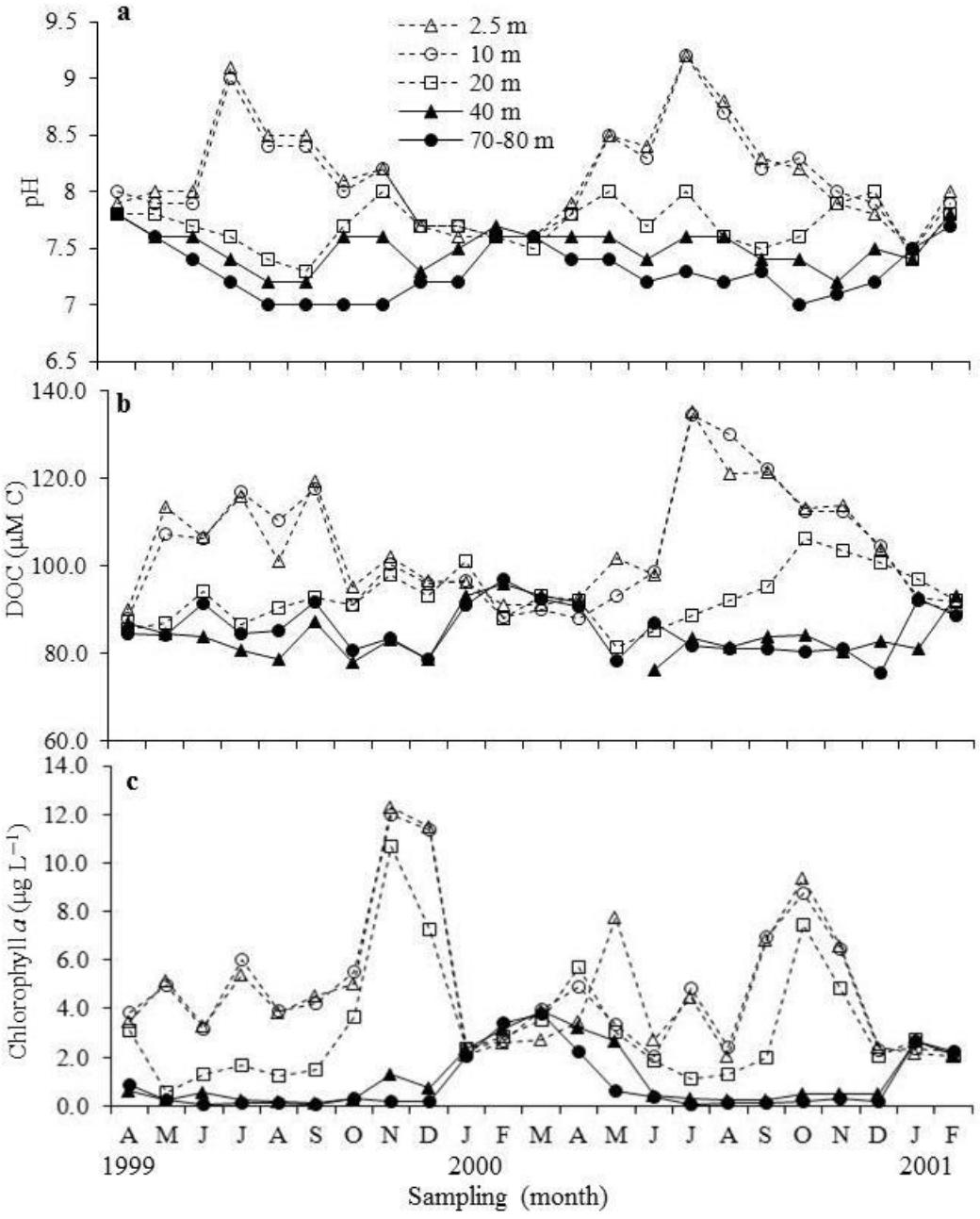

Figure S2. Monthly changes in pH, dissolved organic carbon (DOC) and chlorophyll *a* (Chl *a*) at different water depths (2.5, 10, 20, 40 and 70-80 m) in Lake Biwa, the 11th

largest lake in the world with surface area of approximately 674.8 km^2. Samples were collected monthly during the period of April 1999 to February 2001 at day-time from the northern basin, where the maximum water depth is 104 m (Mostofa et al., 2005). The values of pH and of the concentrations of DOC and Chl *a* gradually increased, reaching a maximum on July (1999 and 2000) for pH, on September (1999) or July (2000) for DOC and on November (1999) or October (2000) for Chl *a*.

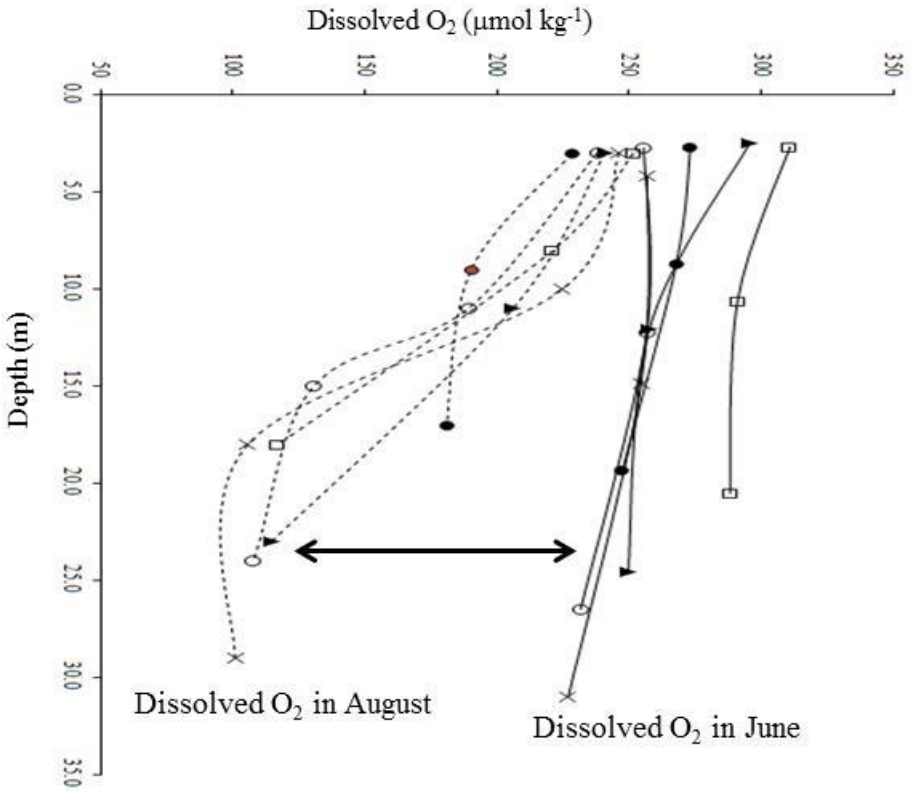

Figure S3. A substantial decline in dissolved O_2 contents in August (dashed lines) compared to June (solid lines) in the seawater of the Yellow Sea. The same symbol indicates the same sampling site for the samples collected during June and August.

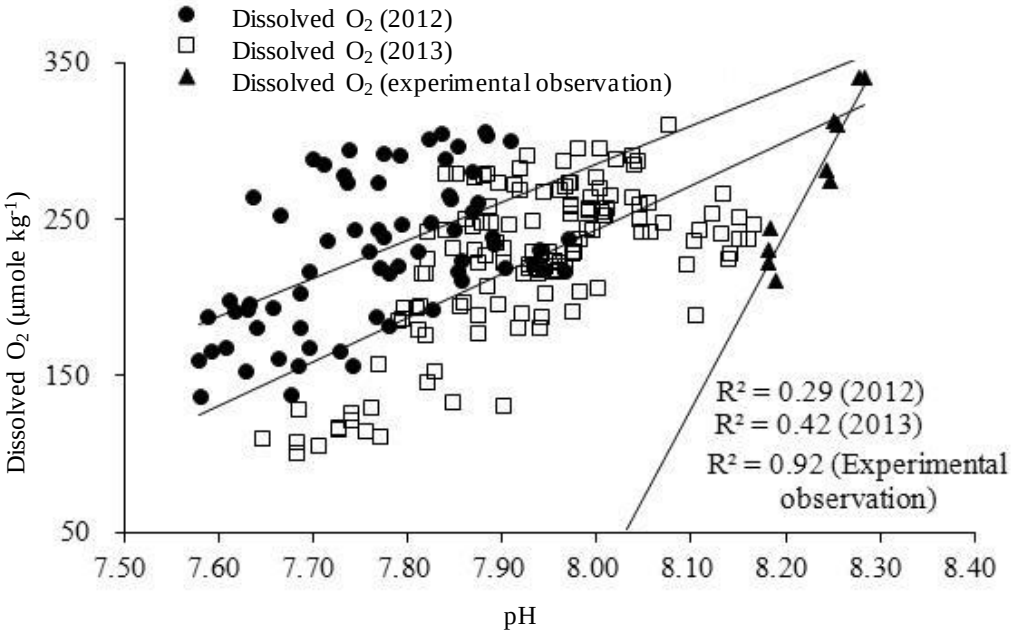

Figure S4. Relationship between pH and dissolved O_2 for a variety of the subsurface seawaters collected from the Yellow Sea in 2012 and 2013. Experiments were carried out on July 2, 2013 using subsurface water collected at 37 m depth from the East China Sea (see the caption of Fig. 4 for a detailed description).

785

Table S1. Ranges of pH, PCO_2, DIC, chlorophyll *a* (Chl*a*), dissolved O_2, hydrogen peroxide (H_2O_2) and water temperature (WT) in world's oceans.

Sampling	pH		$P CO_2$	DIC	Chl *a*	Dissolved O_2		H_2O_2	WT	References
	Surface water (0-20 m)	Anoxic zone	(µatm)	(µmol kg^{-1})	(µg L^{-1})	Surface water (mg L^{-1})	Anoxic zone	(nM)		
Okinawa Island Seawater (Taira Bay, November)	8.02—8.79 (diurnal)	-	-	-	-	-	-	40-160	21-7-23.7	Arakaki et al., 2005
Okinawa Island Seawater (Taira Bay, January)	8.16—8.25 (diurnal)	-	-	-	-	-	-	40-100	18.8-20.9	Arakaki et al., 2005
Okinawa Island Seawater (Sesoko Island, January)	7.82—8.29 (diurnal)	-	-	-	-	-	-	30-110	17.7-20.2	Arakaki et al., 2005
Nanwan Bay, south coast of Taiwan (5-13 June)	8.04-8.24 (diurnal)	-	227-532	1830-2050	0.20-1.10	2.62-5.74	-	-	22.4-28.4	Jiang et al., 2011*
Coastal seawater, Aodi, northeast of Taiwan (1-5 August)	7.87-8.35 (diurnal)	-	178-582	1750-2090	0.30-1.30	2.70-6.56	-	-	25.0-28.0	Jiang et al., 2011*
Coastal seawater (Bay of Bengal, Stn 3)	8.12-8.37 (diurnal)	-	153-373	-	12.35±2.23	-	-	-	28.50-31.70	Akhand et al., 2013
Marine bathing waters (Southern California, USA)	~7.37-8.18 (diurnal)	-	-	-	-	-	-	5-370	18.6-22.5	Clark et al., 2010*
Inner shelf of southern Monterey Bay, California coast	7.7-8.1 (diurnal)	-	-	-	-	2.0–4.6	-	-	9.5-13.5	Booth et al., 2012*
Tampa Bay	7.95-8.24 (diurnal)	-	262-580	-	-	-	-	-	26.2-28.7	Yates et al., 2007
Florida Bay	8.17-8.39 (diurnal)	-	260-497	-	-	-	-	-	23.8-27.3	Yates et al., 2007
Belgian coastal seawater (near Zeebrugge)	8.314-8.358 (diurnal)	-	190-214	-	12.5-23.5	-	-	-	9.74-10.15	Borges and Frankignoulle, 1999*
Seawater, Jarvis Island	7.985-8.019 (diurnal)	-	-	-	-	-	-	-	-	Price et al., 2012
Great Barrier Reef, Lizard Island (subsurface: within 5 cm of the surface)	7.93-8.23 (diurnal)	-	-	-	-	-	-	-	-	Gagliano et al., 2010
Great Barrier Reef, Lizard Island (*Pocillopora damicornis*)	7.93-8.30 (diurnal)	-	-	-	-	-	-	-	-	Gagliano et al., 2010
Great Barrier Reef, Lizard Island (*D. perspicillatus* algal garden)	7.95-8.25 (diurnal)	-	-	-	-	-	-	-	-	Gagliano et al., 2010
Great Barrier Reef, Lizard Island (open sand: within 3 cm of the sand)	7.80-8.24 (diurnal)	-	-	-	-	-	-	-	-	Gagliano et al., 2010
Great Barrier Reef, Heron Island	7.69-8.44 (diurnal)	-	-	-	-	0.46-7.59	-	-	22.2-32.0	Santos et al., 2011
Luhuitou fringing reef, Sanya Bay, South China Sea (winter)	~7.95-8.07 (diurnal)	-	~380-500	-	-	~5.0-8.0	-	-	24.5±0.5	Zhang et al., 2013*
Luhuitou fringing reef, Sanya Bay, South China Sea (spring)	~7.96-8.14 (diurnal)	-	~290-460	-	-	~5.5-8.0	-	-	33.8±0.1	Zhang et al., 2013*
Luhuitou fringing reef, Sanya Bay, South China Sea (summer)	~7.86-8.07 (diurnal)	-	~350-605	-	-	~3.5-7.2	-	-	29.5±0.6	Zhang et al., 2013*
Luhuitou fringing reef, Sanya Bay, South China Sea (autumn)	~ 7.94-8.18 (diurnal)	-	~245-495	-	-	~5.3-10.7	-	-	26.3±1.0	Zhang et al., 2013*
Seawater, Kingman Reef (site Palmyra Terrace North)	7.926 -8.031 (diurnal)	-	-	-	-	-	-	-	-	Price et al., 2012
Seawater, Kingman Reef (site Palmyra Terrace South)	7.901 -8.017 (diurnal)	-	-	-	-	-	-	-	-	Price et al., 2012
Seawater, Kingman Reef (site Palmyra Forereef North)	7.944 -8.007 (diurnal)	-	-	-	-	-	-	-	-	Price et al., 2012
Seawater, Kingman Reef (site Palmyra Forereef South)	7.979 -8.007 (diurnal)	-	-	-	-	-	-	-	-	Price et al., 2012
Seawater, Kingman Reef (site Kingman Reef)	8.021-8.028 (diurnal)	-	-	-	-	-	-	-	-	Price et al., 2012
Coral reef, Ishigaki Island, Japan	7.9-8.4 (diurnal)	-	-	-	-	-	-	-	-	Kayanne et al., 2005
Coral reef, Rukan-sho, Ishigaki Island, Japan (site 1, October)	7.848-8.556 (diurnal)	-	151-900	1460-2103	-	1.81-13.37	-	-	26.4-30.2	Ohde and van Woesik, 1999
Coral reef, Rukan-sho, Ishigaki Island, Japan (site 1, September)	7.951-8.688 (diurnal)	-	68-770	1181-2095	-	-	-	-	27.3-34.2	Ohde and van Woesik, 1999
Reef crest algal community, Ishigaki Island, Japan	7.863-8.335 (diurnal)	-	210-762	-	-	-	-	-	29.84-33.19	Nakamura and Nakamori, 2009
Branching acropora (coral) community, Ishigaki Island, Japan (site 4)	8.030-8.289 (diurnal)	-	201-458	-	-	-	-	-	29.0	Nakamura and Nakamori, 2009
Branching acropora (coral) community, Ishigaki Island, Japan (site 5)	7.818-8.211 (diurnal)	-	271-770	-	-	-	-	-	27.56-30.73	Nakamura and Nakamori, 2009
Branching acropora (coral) community, Ishigaki Island, Japan (site 7)	7.801-8.197 (diurnal)	-	248-799	-	-	-	-	-	27.87-30.62	Nakamura and Nakamori, 2009
Montipora stellata (coral) community, Ishigaki Island, Japan (site 8)	7.773-8.387 (diurnal)	-	144-919	-	-	-	-	-	28.39-33.18	Nakamura and Nakamori, 2009
Pocillopora acropora (coral) community, Ishigaki Island, Japan (site 9)	7.974-8.099 (diurnal)	-	410-569	-	-	-	-	-	30.72-31.25	Nakamura and Nakamori, 2009
Pocillopora acropora (coral) community, Ishigaki Island, Japan (site 10)	7.939-8.113 (diurnal)	-	368-593	-	-	-	-	-	28.27-29.91	Nakamura and Nakamori, 2009
Seawater in the coral reef, Heron Island, Great Barrier Reef	7.96-8.36 (diel)	-	-	1850-2230	-	3.11-7.05	-	-	-	Cyronak et al., 2013*
Uva Reef, Gulf of Chiriqu, Pacific Panamá (dry season)	7.63–8.20 (day)	-	-	-	-	-	-	-	28.8±0.19	Manzello, 2010
Uva Reef, Gulf of Chiriqu, Pacific Panamá (dry season)	7.84-8.04 (night)	-	-	-	-	-	-	-	28.4±0.30	Manzello, 2010

Table S1 (continued)

Sampling	pH		pCO_2	DIC	Chl *a*	Dissolved O_2		H_2O_2	WT	References
	Surface water (0-20 m)	Anoxic zone	(μatm)	(μmol kg^{-1})	(μg L^{-1})	Surface water (mg L^{-1})	Anoxic zone (mg L^{-1})	(nM)		
Uva Reef, Gulf of Chiriqu, Pacific Panamá (wet season)	7.94-8.26 (day)	-	-	-	-	-	-	-	28.9±0.06	Manzello, 2010
Uva Reef, Gulf of Chiriqu, Pacific Panamá (wet season)	7.86-8.01 (night)	-	-	-	-	-	-	-	28.7±0.03	Manzello, 2010
Saboga Reef, Gulf of Panamá (dry season)	7.95–8.08 (day)	-	-	-	-	-	-	-	21.0	Manzello, 2010
Saboga Reef, Gulf of Panamá (wet season)	7.95–8.23 (day)	-	-	-	-	-	-	-	28.6±0.11	Manzello, 2010
Saboga Reef, Gulf of Panamá (wet season)	7.96–8.00 (night)	-	-	-	-	-	-	-	27.5	Manzello, 2010
Reef, Galápagos, Eastern Pacific (cool)	7.65–7.99 (day)	-	-	-	-	-	-	-	25.0	Manzello, 2010
Reef, Galápagos, Eastern Pacific (warm)	7.70–8.07 (day)	-	-	-	-	-	-	-	25.0	Manzello, 2010
Fore reef (benthic), Palmyra (5.86614°N, 162.1172°W)	7.915-8.035 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
Reef terrace (benthic), Palmyra (5.884°N, 162.1218°W)	7.851-8.104 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
Fringing reef (benthic), Moorea (17.4803°S, 149.7989°W)	8.017-8.118 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
Kingman Reef (benthic), Tropical Central Pacific, Open Ocean	8.009-8.034 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
SBC Mohawk Reef (benthic), Kelp (34.3943°N, 119.73°W)	7.700-8.244 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
Coral Reef Lagoon seawater (The Indo-Pacific Oceans)	8.264-8.350	-	292-370	-	-	-	-	-	28.6-30.0	Suzuki and Kawahata, 1999
Coral reef (mesocosm), Moku O Loe, Kaneohe Bay, Hawaii	7.55-8.08	-	500-1950	-	-	-	-	-	-	Kuffner et al., 2008
Seagrass community, Chwaka Bay (Zanzibar, Tanzania)	7.9->8.9 (diurnal)	-	-	-	-	-	-	-	~27.0-33.0	Semesi et al., 2009
Seagrass community, Ishigaki Island, Japan (site 1)	7.763-8.547 (diurnal)	-	111-1085	-	-	-	-	-	30.87-34.32	Nakamura and Nakamori, 2009
Seagrass community, Ishigaki Island, Japan (site 2)	7.894-8.353 (diurnal)	-	204-671	-	-	-	-	-	27.99-33.22	Nakamura and Nakamori, 2009
Seagrass community (*C. nodosa*), Alfacs Bay, Mediterranean (1 m)	8.11-8.59 (diurnal)	-	-	-	-	-	-	-	-	Invers et al., 1997
Seagrass community (*P. oceanica*), Alfacs Bay, Mediterranean (1 m)	8.15-8.45 (diurnal)	-	-	-	-	-	-	-	-	Invers et al., 1997
Seagrass community (*P. oceanica*), Alfacs Bay, Mediterranean (4 m)	8.17-8.34 (diurnal)	-	-	-	-	-	-	-	-	Invers et al., 1997
Benthos community, Ishigaki Island, Japan (site 2)	7.963-8.154 (diurnal)	-	318-540	-	-	-	-	-	28.66-31.61	Nakamura and Nakamori, 2009
Macroalgal Kelp bed (inside), Morbihan Bay, Southern Ocean	8.07-9.11 (diurnal)	-	-	-	-	-	-	-	0.7-15.3	Delille et al., 2000
Macroalgal Kelp bed (outside), Morbihan Bay, Southern Ocean	7.94-8.46 (diurnal)	-	-	-	-	-	-	-	0.7-8.5	Delille et al., 2000
Macroalgae (outside), macroalgal mats, Mediterranean coastal lagoon	8.3-9.0 (diurnal)	-	-	2500-3000	-	-	-	-	-	Menéndez et al., 2001
Macroalgae (inside), macroalgal mats, Mediterranean coastal lagoon	8.4-9.6 (diurnal)	-	-	2500-3000	-	-	-	-	-	Menéndez et al., 2001
Macroalgal habitats, inshore Danish waters (0.2 m)	7.5-9.1 (diurnal)	-	-	-	-	-	-	-	-	Middelboe and Hansen, 2007*
Macroalgal habitats, inshore Danish waters (0.4 m)	7.8-9.0 (diurnal)	-	-	-	-	-	-	-	-	Middelboe and Hansen, 2007*
Macroalgal habitats, inshore Danish waters (0.6 m)	8.0-8.9 (diurnal)	-	-	-	-	-	-	-	-	Middelboe and Hansen, 2007*
Macroalgal Kelp bed, La Jolla (pelagic)	7.970-8.229 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
Southern Ocean surface water (Sta. SIE1)	~8.13-8.17 (diurnal)	-	~280-305	-	-	-	-	-	~(-0.05)-(-0.25)	Fransson et al., 2004*
Southern Ross Sea under Antarctic sea ice (site: Cape Evans)	8.039–8.134 (diel, 15 m)	-	-	-	-	-	-	-	-	Matson et al., 2011
Temperate Eastern Pacific (CCE1), Open Ocean	8.059-8.082 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
Polar seawater (benthic), Cindercones, Antarctic Ocean	8.039-8.134 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
Polar seawater (benthic), Cape Evans, Antarctic Ocean	8.002-8.050 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
Upper Reach of the Pearl River Estuary (South China Sea)	6.98-7.75	-	≤7460	1900-2740	-	0.25-3.61	-	-	~14.5-16.8	Dai et al., 2006
Outer estuary of Yangtze River (East China Sea)	7.76–8.03 (spring)	-	560–800	1575–1840	-	-	-	-	14.6–15.7	Zhai et al., 2007
Outer estuary of Yangtze River (East China Sea)	7.92–8.04 (winter)	-	316–477	1935–1995	-	-	-	-	7.1–15.5	Zhai et al., 2007
Bohai and Liaodong Bay (0 to ~15-20 m)	7.90-8.12 (June)	~7.82-8.04	-	-	-	~7.05-10.16	~7.21-9.51	-	~13.0-18.5*	Zhai et al., 2012
Bohai and Liaodong Bay (0 to ~15-20 m)	7.86-8.17 (August)	~7.64-7.96	-	-	-	~7.21-9.18	~3.28-7.38	-	~19.0-27.0*	Zhai et al., 2012
Yellow Sea: Northern side	7.67—7.92 (winter)	~7.67—7.75	-	-	-	~9.90- (6 m)	-	-	(—1.45)–6.74	Zhai et al., 2014
Yellow Sea: Northern side	7.85—8.11 (spring)	~7.69—7.78	-	-	-	-	-	-	~4.50–13.22	Zhai et al., 2014
Yellow Sea: Northern side	7.86—8.14 (summer)	~7.62—7.92	-	-	-	7.44-9.54 (13-19 m)	-	-	~5.00—24.83	Zhai et al., 2014
Yellow Sea: Northern side	7.76—8.11 (autumn)	7.53—7.60	-	-	-	6.82 (19 m)	-	-	~7.50–18.37	Zhai et al., 2014
East China Sea	8.04-8.22	-	-	1980-2220	-	-	-	-	~12-25	Wang et al., 2000

794 Table S1 (continued)

Sampling	pH		$P CO_2$	DIC	Chl *a*	Dissolved O_2		H_2O_2	WT	References
	Surface water (0-20 m)	Anoxic zone	(μatm)	(μmol kg^{-1})	(μg L^{-1})	Surface water (mg L^{-1})	Anoxic zone	(nM)		
Coastal seawater, Northern South China Sea	< 8.2-8.6	~8.18 (65 m)	-	~1500-1900	-	-	-	-	-	Dai et al., 2008
Seto Inland Sea	8.15-8.26 (0-10 m)	> 7.96 (40 m)	-	~1750-1950	-	~ 6.0-9.5 (0-10 m)	> 3.0 (40 m)	-	~9-26	Taguchi and Fujiwara, 2010*
Coastal seawater (Bay of Bengal)	7.96-8.38	-	416-1062	-	-	-	-	-	26.0-28.0	Biswas et al., 2004
Puget Sound Estuary, main basin (Summer)	8.05	7.83 (> 100 m)	-	1884	-	~ 5.74-8.20	-	-	-	Feely et al., 2010
Puget Sound Estuary, main basin (Winter)	7.71	7.73 (> 100 m)	-	1985	-	8.2	-	-	-	Feely et al., 2010
North Sea (English Coastal waters)	~8.10-8.16	-	-	-	-	~4.07-4.66	-	-	-	Frankignoulle et al., 1996*
North Sea (French coastal waters)	~8.10-8.50; ~7.95-8.28	-	-	-	-	~3.69-6.39; 3.77-4.18	-	-	-	Frankignoulle et al., 1996*
Northern Gulf of Mexico (summer)	> 8.2	< 7.6-8.0	-	-	-	-	-	-	-	Cai et al. 2011*
Northern Gulf of Mexico (spring)	> 8.2	7.8-8.2	-	-	-	-	-	-	-	Cai et al. 2011*
Northern Gulf of Mexico	8.10-8.18 (1-2 m)	7.71-7.93 (10-37 m)	-	-	-	5.48-6.10	0.10-2.79	-	23.0-31.2	Sunda and Cai, 2012
Monterey Bay L20 (pelagic), near Shore	7.857-8.356 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
Upwelling seawater (pelagic), Pt. Conception, Monterey Bay	7.869-8.266 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
Upwelling seawater (pelagic), Pt. Ano Nuevo, Monterey Bay	7.685-8.152 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
North Pacific Ocean (25-55°N, 152°W)	8.2-7.6	~7.6-7.3 (> 500)	-	-	-	-	-	-	-	Byrne et al. 2010
Southern Ocean (Atlantic sector)	8.060-8.123	-	313-377	-	-	5.31-5.89	-	-	~(—2)—13.8	Chierici et al., 2004*
Southern Ocean (Atlantic sector)	~8.06-8.12	-	~313-377	-	~0.2-1.0	-	-	-	-	Chierici et al., 2004*
Cold-water, northeast Atlantic (5 sites: depths 0-1930 m)	< 8.10-8.19	> 7.92-8.06	-	-	0.02-1.2	-	-	-	-	Findlay et al., 2014
Submarine spring, Puerto Morelos, Mexico	7.143-8.048 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
CO_2 vent, Ischia (South Zone), Italy	6.699-8.129 (30 days)	-	-	-	-	-	-	-	-	Hofmann et al., 2011
CO_2 vent, off Ischia Island, Italy (surface water at site S1)	8.13-8.17 (21 days)	-	304-346	2120-2160	-	-	-	-	18.0-19.7	Hall-Spencer et al., 2008
CO_2 vent, off Ischia Island, Italy (surface water at site S2)	7.35-8.16 (21 days)	-	314-2,626	2120-2510	-	-	-	-	17.8-20.0	Hall-Spencer et al., 2008
CO_2 vent, off Ischia Island, Italy (surface water at site S3)	6.07-7.37 (21 days)	-	2,448-51,997	2510-4220	-	-	-	-	18.0-20.0	Hall-Spencer et al., 2008
CO_2 vent, off Ischia Island, Italy (surface water at site N1)	7.96-8.19 (21 days)	-	286-552	2100-2240	-	-	-	-	18.0-20.0	Hall-Spencer et al., 2008
CO_2 vent, off Ischia Island, Italy (surface water at site N2)	7.54-8.17 (21 days)	-	309-1,644	2130-2440	-	-	-	-	18.0-20.0	Hall-Spencer et al., 2008
CO_2 vent, off Ischia Island, Italy (surface water at site N3)	6.31-7.90 (21 days)	-	654-29,885	2280-3500	-	-	-	-	18.0-20.0	Hall-Spencer et al., 2008
CO_2 vent, off Ischia Island, Italy (at site P1 on 3 m depth)	8.15-8.18 (21 days)	-	296-322	2110-2130	-	-	-	-	18.1-20.0	Hall-Spencer et al., 2008
CO_2 vent, off Ischia Island, Italy (at site P2 on 3 m depth)	8.13-8.20 (21 days)	-	278-347	2100-2160	-	-	-	-	18.5	Hall-Spencer et al., 2008
CO_2 vent, off Ischia Island, Italy (at site P3 on 3 m depth)	7.67-8.16 (21 days)	-	315-1,173	2130-2390	-	-	-	-	19.0-19.5	Hall-Spencer et al., 2008
CO_2 vent, off Ischia Island, Italy (at site P4 on 3 m depth)	6.98-8.14 (21 days)	-	334-6,253	2140-2670	-	-	-	-	19.0-19.5	Hall-Spencer et al., 2008
Hiroshima Bay, Japan	-	-	-	-	-	-	-	143-448	19.5-22.1	Akane et al. 2004
Hiroshima Bay, Japan	-	-	-	-	-	-	-	0-195	-	Sakugawa et al., 2000
Iyo-Nada Bay, Japan	-	-	-	-	-	-	-	7-146	-	Sakugawa et al., 2000
Seto Inland Sea, Japan	-	-	-	-	-	-	-	40-191	-	Sakugawa et al., 1995
Tokyo Bay	-	-	-	-	-	-	-	20-207	-	Sakugawa et al., 1995
Sagami Bay	-	-	-	-	-	-	-	40-80	-	Sakugawa et al., 1995
Mediterian, Israeli coastal waters	-	-	-	-	-	-	-	10.0-80.0	-	Herut etal., 1998
Red Sea, Gulf of Aqaba	-	-	-	-	-	-	-	8-100	-	Herut etal., 1998
Lagrangian, Atlantic Ocean	-	-	-	-	-	-	-	23-55	-	Yuan and Shiller, 2001
Underway, Atlantic Ocean	-	-	-	-	-	-	-	27-47	-	Yuan and Shiller, 2001
Bermuda Atlantic Time Series Station	-	-	-	-	-	-	-	25-84	-	Avery Jr. et al., 2005

The dissolved O_2 values measured at different units adjusted using 1 ml $L^{-1} \approx 1.4$ mg L^{-1} at 20 psu and 2 mgO_2 $L^{-1} \approx 61$ molO_2 kg^{-1} (Gray et al., 2002).

795 *Data extracted from the graph.

796