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REVIEW ARTICLE

OCEAN ACIDIFICATION AND ITS IMPACTS ON THE MARINE BIODIVERSITY

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ABSTRACT

Ocean acidification is roughly emerged as one of the largest threats to marine organisms and ecosystems. Average global surface ocean pH has already fallen from a pre-industrial value of 8.2 to 8.1, corresponding to an increase in acidity of about 30%. Values of 7.8–7.9 are expected by 2100, representing a doubling of acidity. The ocean has absorbed between 24 and 34% of anthropogenic CO_2 emissions during the past 5 decades. The massive input of CO_2 generates sweeping changes in the chemistry of seawater, especially on the carbonate system. Acidification alters seawater chemical speciation and biogeochemical cycles of many elements and compounds. One well-known effect is the lowering of calcium carbonate saturation states, which impacts shell-forming marine organisms from plankton to benthic molluscs, echinoderms, and corals. Decreases in the availability of carbonate ions force marine organisms to spend more energy building and maintaining their shells or skeletons. For some organisms, spending more energy on shell formation may leave less energy for other biological processes like growing, reproducing or responding to other stresses. Many shell-forming marine organisms are very sensitive to changes in pH and carbonate ion concentrations; conditions predicted for the coming decades may prove very stressful to these calcifying organisms. Corals, bivalves (such as oysters, clams, and mussels), pteropods (free-swimming snails) and certain phytoplankton species fall into this group. The biological impacts of ocean acidification will vary, because different groups of marine organisms have a wide range of sensitivities to changing seawater chemistry. Impacts from ocean acidification at any life stage can reduce the ability of a population to grow or to recover from losses due to disturbance or stress. Therefore ocean acidification will also impact various economic sectors (eg: fisheries, aquaculture, tourism and coastal communities) and may also have heavy indirect effects on much broader segment of the world economy and production. Ocean acidification represents yet another stress on marine environments that may endanger the flow of goods and services to marine-dependent communities. The atmospheric CO_2 can be controlled by avoiding anthropogenic activities such as fossil fuel burning and deforestation. The mitigation approach for ocean acidification includes addition of lime and iron fertilization which could neutralize the acidity and increase the ocean productivity.

INTRODUCTION

Although coastal and surface waters make up only a small portion of the world's oceans, they are focal points for ocean production and human activity; therefore, understanding pH changes in these areas is crucial (Wootton *et al*. 2008). Ocean acidification refers to the ongoing decline in oceanic pH resulting from the uptake of atmospheric CO_2 (Albright, *et. al.,* 2010). The rising concentration of CO_2 in Earth's atmosphere is changing the carbonate chemistry of the ocean (Cohen, *et. al.,* 2009). In the oceans, CO_2 dissolved in seawater exists in three main inorganic forms collectively known as dissolved inorganic carbon (DIC). The CO_2 budget of the ocean comprises about 1% physically dissolved CO_2, including H_2CO_3, as well as about 91% bicarbonate (HCO_3^-) and about 8% carbonate (CO_3^{2-}) (Portner, 2008). Average global surface ocean pH has already fallen from a pre-industrial value of 8.2 to 8.1, corresponding to an increase in acidity of about 30%. Values of 7.8–7.9 are expected by 2100, representing a doubling of acidity (Blackford, *et al.,* 2007). The ocean has absorbed between 24 and 34% of anthropogenic CO_2 emissions during the past 5 decades. Although it affects a broad range of marine species, those that build a shell or skeleton out of calcium carbonate appear especially vulnerable. Diminished $CaCO_3$ saturation state leads to a reduction of calcification rates at the organism level in many species of the most important calcifying groups in the ocean, i.e., in coccolithophorids, foraminifera, and corals by up to 83% (Ilyina *et. al.,* 2009). Therefore ocean acidification will also impact various economic sectors (eg: fisheries, aquaculture, tourism and coastal communities) and may also

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have heavy indirect effects on much broader segment of the world economy and production. Ocean acidification represents yet another stress on marine environments that may endanger the flow of goods and services to marine-dependent communities.

Mechanism of ocean acidification

Atmospheric CO_2 level is increased by various human activities such as fossil fuel burning, deforestation and land use change. When CO_2 dissolves in the seawater it increases concentrations of hydrogen ion [H^+], lowering ocean pH. The increased CO_2 diffuses from the atmosphere into ocean surface waters, resulting in increased partial pressure of CO_2 and reduced carbonate ions (CO_3^{2-}) (Kurihara, 2008). This reduction in ocean pH has some direct effect on marine organisms. Furthermore, some of this additional [H^+] reacts with carbonate ions [CO_3^{2-}] to form [HCO_3^-]. The decrease in carbonate ion decreases the saturation state of calcium carbonate minerals, making it more difficult for calcifying marine organisms to form their shells and skeletons (Cao *et al.,* 2007). The carbonate ion is one of the building blocks of calcium carbonate ($CaCO_3$) and changes in its ambient concentration can thus affect the ability of calcifying organisms to precipitate $CaCO_3$ (Gazeau, *et. al.,* 2007). Many important groups of marine organisms have a skeleton of calcium carbonate, which dissolves when it reacts with free hydrogen ions (Wootton *et al*. 2008).

Factors contributing ocean acidification

Atmospheric pCO_2 controls air-sea equilibrium of CO_2. Temperature and pressure determines the CO_2 solubility in the oceanic surface water. Upwelling is one of the factor which delivers CO_2 rich deep water to the sea surface. Calcium carbonate dissolution is the process which will increase the CO_2 concentration in water and also decrease the alkalinity of the water. Biological processes such as photosynthesis and respiration play a major role in CO_2 budget regulation by removing and releasing CO_2 from the water. Calcification is the process where the excess CO_2 is to be precipitated for the shell formation of calcifying organisms (Kleypas, *et. al.,* 2006).

Ocean chemistry

Ocean is considered to be carbon reservoir, which absorbs roughly one-third of the CO_2 that humans release into the atmosphere annually. Increase in the hydrogen ion concentration will decrease the saturation state of calcium carbonate (Kurihara, 2008). Calcification rate decreased with ocean acidification (Kelly and Hofmann, 2013) which will decrease the deepwater carbon storage and may deplete the buffering capacity of the ocean (Wootton *et al*. 2008). Thus ocean acidification is changing the ocean chemistry by altering the carbonate system.

Biogeochemical processes

Beman *et al*., (2011) reported that ocean acidification could reduce nitrification rates by 3–44% within the next few decades, affecting oceanic nitrous oxide production, reducing supplies of oxidized nitrogen in the upper layers of the ocean and fundamentally altering nitrogen cycling in the sea. The rate of nitrification drops drastically with decreasing pH (Liu *et al*., 2010).

Calcification

The carbonate concentration and saturation levels of calcium carbonates in seawater are widely reported to set calcification rates (Pörtner, 2008). With increasing dissolved CO_2, seawater chemistry eventually crosses the threshold for the saturation states of aragonite and calcite (two mineral phases of calcium carbonate) that support biogenic calcification. These forms begin to dissolve in low-pH environments, leading to a net loss of calcareous structures exposed to seawater or severe reductions in calcification and growth rates (Anthony *et al*., 2008 and Fabry *et al*., 2008). $CaCO_3$ seems to ballast faecal pellets, increasing rates of sinking and so decreased calcification could lead to decreased rates of deep-water carbon storage (Kelly and Hofmann, 2013).

Calcifying organisms

The oceanic uptake of anthropogenic CO_2 and the concomitant changes in seawater chemistry have adverse consequences for many calcifying organisms and may result in changes to biodiversity, trophic interaction and other ecosystem processes (Kleypas *et al*., 2006). Little information is available for other important taxa, for processes other than calcification or for potential ecosystem-level consequences emerging from the oceanic pCO_2 levels that are predicted to occur over the next 100 years (Fabry *et al*., 2008). Many calcifying species exhibit reduced calcification and growth rates in laboratory experiments under high-CO_2 conditions (Doney *et al*., 2009). Coccolithophores are unicellular algae covered in calcitic plates found throughout most of the world's oceans. This group plays an important role in global geochemical cycles and so estimating changes in calcification rates is important for forecasting changes in future global carbon cycles Thus, if increased dissolved CO_2 leads to decreased calcification, there should be a negative feedback, where increased atmospheric CO_2 leads to decreased CO_2 production by Coccolithophores (Kelly and Hofmann, 2013). Foraminifera such as *Orbulina universa* and *Globigerinoides sacculifer* are showing reduction in their shell mass when pCO_2 is about 560–780 ppmv (Fabry *et al*., 2008).

Larvae of marine species

Larvae were substantially more vulnerable to elevated CO_2 than juvenile stages (Talmage and Gobler, 2009, 2010 and 2011). They experimented Two life history stages (larval, juvenile) of three species of calcifying bivalves (*Mercenaria mercenaria, Crassostrea virginica, and Argopecten irradians*) under CO_2 concentrations (250, 390, and 750 ppm) representative of past, present, and future summer conditions. Larval brittle star, *Ophiothris fragilis*, showed 100% mortality when pH of water goes 7.7 and 7.9 (Dupont *et al*., 2008). Larval sand dollars *Dendraster excentricus* showed induced morphological changes when reared in a pCO_2 concentration of 1000ppm and larvae had narrower bodies and smaller stomachs and shorter arms. Previous modeling and experimental observations have suggested that such changes in larval morphology are likely to alter swimming performance (Chan *et al*., 2011). Planktonic larvae of many marine invertebrates also possess calcified structures, including shells of molluscan veligers, skeletal rods of echinoplutei and posterior ossicles of auricularia. These calcifying larval stages are likely to be sensitive to changes in ocean pH and some species are known to be highly sensitive. Decreased calcification at larval and settlement stages is considered to affect their fitness and increase mortality (Kurihara, 2008).

Effect on calcified marine species to predation

Many marine species rely on these calcium carbonate shells as defense from predators. Although shells protect molluscs from physical stresses, including heat, desiccation and wave forces, they function primarily as a defense against predators. A reduction in size is a common response in molluscs exposed to ocean acidification. Predators would thus receive substantially less energy per mussel consumed and would need to consume more individuals to maintain their energetic needs. Likewise, the total lipid content of larval bivalves has been found to decrease with ocean acidification. Increased metabolic rates could also result in slower growth or reduced body sizes among predators whether they were calcified or not. Many predator-prey interactions are size structured and a reduction in predator size could reduce the preferred prey size as well. In addition, reduced predator size could reduce the size of prey that a predator is able to successfully capture and consume or increase its handling time of prey (Kroeker *et al*., 2014).

Benthic invertebrates

Gazeau *et al*., (2007) reported that calcification rates in the mussel *Mytilus edulis* and the Pacific oyster *Crassostrea gigas* decreased by 25% and 10%, respectively, when grown at ∼740 ppmv CO_2. Similarly, reduced shell growth was observed in the gastropod *Strombus luhuanus* and two sea urchin species when grown at 560 ppmv CO_2 over a 6-month period (Shirayama & Thorton 2005).

Early life stages of invertebrates

CO_2 is expected to impact the life cycles of benthic calcifiers in different ways under increasing levels (380~2000 μatm pCO_2/ pH 8.2~7.3). The effects of high pCO_2 in seawater are anticipated to occur in several different life stages, including egg, cleavage, larva, settlement, juvenile and adult stages, which are consequently likely to impact the distribution and abundance of benthic calcifiers. Impacts on fertilization and reproduction can directly affect population size and decrease the calcification at larval and settlement stages is considered to affect their fitness and increase mortality. Cumulative effects across different life stages may lead to species extinctions. Although most calcifiers were affected at pCO_2 values >1000 μatm (pH 7.9~7.7), copepods appear less sensitive to elevated pCO_2 conditions. The fertilization rate of *Echinometra mathaei* was observed to be more affected than that of *Hemicentrotus pulcherrimus* at the same pCO_2 level (Kurihara, 2008).

Coral

Ocean acidification may negatively impact the early life stages of some marine invertebrates including corals. Although reduced growth of juvenile corals in acidified seawater has been reported, coral larvae have been reported to demonstrate some level of tolerance to reduced pH. The oxygen consumption of *Acropora digitifera* larvae tended to be suppressed with reduced pH. Results also showed that the metamorphosis rate significantly decreased under acidified seawater conditions after both short (2 h) and long (7 d) term exposure at three different pH levels (8.0, 7.6, and 7.3) suggesting that suppressed metabolism and metamorphosis may alter the dispersal potential of larvae and subsequently reduce the resilience of coral communities in the near future as the ocean pH decreases (Nakamura *et al*., 2011). Ocean acidification triggers the coral bleaching (expulsion of algal endosymbionts and subsequent loss of productivity and/or death of the host) (Kelly and Hofmann, 2013). It induces loss of habitat complexity in coral reef ecosystems and subsequent losses in coral reef biodiversity (Nakamura *et. al.,* 2011).

Seagrass ecosystem

Ocean acidification may have dramatic effects on the diversity of seagrass habitats and lead to a shift in the biogeochemical cycling of both carbon and carbonate in coastal ecosystems dominated by seagrass beds. Seagrasses could also benefit from the exclusion of epibionts. Since the presence of epibionts on their blades can reduce their photosynthetic rate both by acting as a barrier to carbon uptake and by reducing light intensity (Martin *et al.,* 2008).

Impact on host-parasite interaction

Parasite-host interactions are a specialized form of predator-prey interactions that might also be influenced by ocean acidification through energetic trade-offs. Coastal molluscs are host to a variety of parasites, from trematode flatworms to nematodes and gregarine protozoans. Among molluscs, phagocytosis is a common defense against small parasites, including the sporocytic stage of trematodes. An initial study of immune responses in the blue mussel *Mytilus edulis* found a reduction in phagocytic activity in high CO_2, suggesting a suppression of the immune system with ocean acidification (Kroeker et al., 2014).

Impact on otolith of marine finfish

Ocean acidification has a graded effect on cobia otoliths (2,100 μatm partial pressure of carbon dioxide (pCO_2) significantly increased not only otolith size (up to 49% greater volume and 58% greater relative mass) but also otolith density (6% higher)), with the potential to substantially influence the dispersal, survival and recruitment of a pelagic fish species (Bignami *et al*., 2013). Sound detection could be magnified due to an increase in otolith size, but it is unclear whether increased sound detection improves or worsens fish's ability to detect prey (or predators). This outcome may depend on whether fish can discriminate useful sounds from background noise (Kroeker *et al.,* 2014).

Beneficial impacts

There are marine organisms, mostly photosynthetic, that genuinely do seem to benefit from ocean acidification under experimental conditions. These include seagrasses, some non-calcifying phytoplankton (microalgae and cyanobacteria) and several other microbial groups. These might benefit directly, by CO_2-enhancement of photosynthesis, or indirectly, if predators and competitors are reduced in abundance (Williamson and Turley, 2012). It seems that elevated CO_2 conditions can cause an increase in the growth and abundance of non-calcareous algae and this deserves more attention (Connell and Russell, 2010).

Mitigation approach

Although iron fertilization and addition of lime neutralizes the pH of the ocean and thus increases the overall ocean productivity, but these two practices is not practical. Natural Resources Defense Council (NRDC) suggesting that reducing the CO_2 emissions into the atmosphere is the only practical way to minimize the future ocean acidification. There are several ways to reduce the CO_2 emissions such as exploration of transportation alternatives, choosing an efficient vehicle, replacing incandescent bulbs with CFLs (utilizes only 25% energy when compared with other bulbs), using green gardening techniques (short-term solution to the progression of ocean acidification in some places) and Protecting mangroves and seagrass meadows.

Conclusions

Future changes in ocean acidity will potentially impact the population size and dynamics, as well as the community structure of calcifiers, and will therefore have negative impacts on marine ecosystems (Kurihara, 2008). Ocean acidification leads to changes in marine carbonate chemistry that are predicted to cause a decline in future coral reef calcification (Shaw *et al.,* 2012). There are several organisations working for addressing the effect of ocean acidification on marine finfish and shellfish. We have only begun to generate the data needed to assess CO_2-driven impacts on organisms and ecosystems in the geologic past and to anticipate the effects of anthropogenic ocean acidification in the decades and centuries ahead.

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