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Ocean Acidification: an impending disaster to benthic shelled invertebrates and ecosystem

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ABSTRACT

Ocean acidification (OA) is posing a significant threat to marine biodiversity and ecosystem functioning. This review highlights the current state of knowledge and gaps on biological responses of benthic shelled invertebrates to OA. A substantial research accomplished during the last decade demonstrated that the key invertebrates such as corals, oysters, mussels, crustaceans, echinoderms would be severely affected by this phenomenon in the near future. The effects are varied among taxa and life stages within taxa; heavily calcified (mussel, oyster, gastropods) are more sensitive than less calcified invertebrates (crabs, copepods, tanaids), and larval stage are more vulnerable than adult stage. When all taxa are considered together, OA has a significant negative effect on calcification, growth and survival, development and abundance. Most of the studies conducted *in vitro* for short-term basis using single species and single stressor which may not reflect the real ecosystem scenario. Experiments combining multiple stressors (temperature, hypercapnia, hypoxia, nutrients) have just been initiated. Still, field data at community and ecosystem level are lacking. The variety of biological response observed at the organism level might prevent extrapolation at the community and ecosystem level. Therefore, for improved comprehension of marine ecosystem response to OA needs manipulative experiments on the community level.

Key words**:** ocean acidification; pH; biodiversity; invertebrates; benthic ecosystem.

1. INTRODUCTION

Ocean acidification (OA), is one of the major drivers of ongoing global environmental change which cause a global scale disturbance to marine ecosystems damaging biodiversity and hampering proper ecosystem functioning (Orr et al., 2005; Kroeker et al., 2011; Cichowska & Kosakowska, 2014). OA refers to a reduction in the pH and CO_3^{2-} level of marine waters due to the absorption of anthropogenic atmospheric CO_2 by ocean surface. Since the beginning of industrial period, the atmospheric global average level of CO_2 has increased from~280 ppm to nearly 385 ppm (Fig. 1) due to burning of fossil fuel by human and is modelled to increase to 500–1,000 ppm by the end of this century (IPCC, 2007; Feely et al., 2009). This excess level of atmospheric CO_2 is naturally diffused to surface ocean to offset the level between air and sea (Fig. 2). An estimate suggest that ~30% of recently emitted CO_2 has been absorbed by the ocean to date (Feely et al., 2009) and chemically, this absorbed CO_2 reacts with seawater releasing hydrogen ion (H+), and cause a reduction in pH and ultimately decreases the levels of carbonate ion (CO_3^{2-}) (Fig. 2). This process results in OA and is projected to decrease the pH of oceanic surface waters by 0.3 to 0.4 pH units by the end of 2100 (Orr et al., 2005). It is predicted that over the next three centuries, increasing atmospheric CO_2 of nearly 2000 ppm can drive the ocean pH down to ~ 0.77 units at a rate of change faster than any experienced in the last 300 million years (Caldeira & Wickett, 2003). These dramatic changes in ocean chemistry could therefore drive dissolution of carbonate structures of many marine organisms (e.g., shell fish and finfish) having calcium carbonate shells, skeletons, or internal structures (e.g., otoliths and statoliths) (Fabry et al., 2008), and will reduce such species' ability to make their shells. Failure to produce skeleton/carbonate structure in a changing ocean has negative implications for a diversity of marine species. Thus OA poses a significant threat to marine biodiversity and ecosystems.

Marine ecosystems are extremely important to humankind providing >60 % of the value of ecosystem services derived from the nature (Costanza et al., 1997). It provides diverse habitat for 80 % of the earth's organisms and produces 50 % of the oxygen in the atmosphere, fixes 50 % of the global primary production (Turley and Gatusso, 2012). Millions of people are depended on ocean for their food and livelihood. The coastal ecosystems (e.g., coral reefs, mangroves, sea grass and kelp beds) protects shorelines. For example, tropical coral reef ecosystems provide food, income, and coastal protection for around 500 million people throughout tropical coastal areas of the world, and they have an estimated annual value of US$30 billion with the protective function of reefs to shorelines valued at US$9 billion per annum (Cooley et al., 2009). But future OA will cause a significant ecological threat to marine organisms globally.

Majority of the economically and ecologically benthic invertebrate comprise calcifying organisms (e.g., cnidarians, mollusks, crustaceans and echinoderms). Lowenstam and Weiner (1989) reported nine multicellular invertebrate phyla have benthic representatives with $CaCO_3$ skeletal hard parts. Until recently most of the OA studies have focused on these calcifying marine invertebrate species because altered carbonate chemistry due to OA has direct implications (e.g., shell dissolution) for their calcification processes (Orr et al., 2005; Fabry et al., 2008). So, benthic faunal studies relating to OA are indispensable for proper understanding and management of any aquatic ecosystem.

Provided that a significant proportion of the global human population is directly or indirectly dependent on the ecosystem goods and services delivered by the ocean (e.g. for food security, employment, tourism), so to predict the future vulnerability of marine ecosystems to OA, it is important to have a strong understanding of the rate to which OA impacts physiological processes such as photosynthesis, respiration, and nutrient dynamics. These processes are important drivers for calcification, ecosystem structure, biodiversity, and the health of the ocean. To date we do not know how many of these essential processes will be impacted by future OA.

This contribution aim to highlight the current state of knowledge on the biological response of benthic shelled invertebrates and ecosystem to OA. In addition, we will focus the current gaps in our understanding and the need for future research.

2. MATERIALS AND METHODS

Studies related to biological response of benthic invertebrates to OA or low pH have been searched through the internet search engine 'Google Scholar', 'Scopus' and 'Science Direct' data base. Only peer-reviewed papers published from January, 2004to December, 2013 have been considered, which made an obvious reference list to ocean acidification. We confined our search to the last decade as a substantial work on biological responses of OA has been performed since the year, 2004, immediately after the term 'OA' was first coined by Caldeira & Wickett (2003). The search terms included a separate or combination terms of 'Ocean acidification', 'pCO_2 and Ocean', 'pH and Ocean','CO_2 and marine invertebrates', 'pH and marine ecosystems', 'CO_2 and marine ecosystem', 'Climate change and ocean' 'Coastal ecosystems'. Additional papers were tracked by cross referencing.

3. RESULTS AND DISCUSSION

3.1. Impacts on benthic invertebrates

The predicted OA has been shown to negatively influence a diverse group of marine benthic invertebrates, including corals (Albright et al., 2010; Anthony et al., 2008), oyster (Miller et al., 2009; Beniash et al., 2010; Parker et al., 2010), mussel (Bechmann et al., 2011; Berge et al., 2006, Gazeau et al., 2007), clam (Green et al., 2004), abalone (Byrne et al., 2011; Crim et al., 2011), gastropod (Marshall et al., 2008; Kimura et al., 2011) crab (Long et al., 2013) and echinoderms (Kurihara and Shirayama, 2004; Dupont et al., 2008; Brennand et al., 2010; Byrne et al., 2011) (Table 1). The impacts are varied and diverse ranging from: significantly negative to positive, individual species to community, larval to adult stage, developmental to physiological process. The effects are also differed among taxa and life stages within taxa. For example, heavily calcified (mussel, oyster, gastropods) are more sensitive than less calcified invertebrates (crabs, copepods, tanaids), and larval stage are more vulnerable than adult stage (Kroeker et. al., 2010). When all taxa are considered together, OA had a significant negative effect on calcification, recruitment, growth, survival, development and abundance (Table 1).

The responses of marine organisms to future oceanic acidification have recently been thoroughly reviewed by some other major reviews and meta analyses (Guinotte & Fabry, 2008; Fabry et al., 2008; Doney et al., 2009; Hendriks et al., 2010; Kroeker et al., 2010; Hoffmann et al., 2010; Kroeker et al., 2013; Gazeau et al., 2013; Harvey et al., 2013; Cichowska & Kosakowska, 2014). Studies have mostly focused on calcifying marine invertebrate species, as marine carbonate chemistry and pH are known to play important roles in key physiological processes (e.g., calcification process) that ultimately influence their behavior, growth, development and survival (Pörtner, 2008; Fabry et al., 2008; Kroeker et al., 2013; Harvey et al., 2013). For these calcifying organisms to build their carbonate structures, seawater has to be supersaturated in calcium carbonate. But acidification leads to reduce the carbonate saturation of the sea water, making calcification by organisms more difficult and stimulating dissolution of structures already formed. Feely et al. (2004) reported that the aragonite and calcite saturation horizons of the world's oceans are becoming shallower (i.e., shoaling) due to the rapid uptake of human-generated CO_2. Future estimates of aragonite saturation horizon depth indicate that shoaling will occur in the North Pacific and Southern Ocean within this century (Orr et al., 2005). Susceptibility to acidification is depended on whether the crystalline form of their calcium carbonate is aragonite or calcite. Aragonite is more soluble under acidic conditions than calcite, making it more susceptible to dissolution in acidic sea water.

OA causes two-fold problem for a species with calcium carbonate structures: (1) exposed shells may start to dissolve if saturation states drop low enough (Rodolfo-Metalpa et al., 2010) and (2) individuals would have to spend more energy to retain their shells due to unsaturated carbonate concentrations in water (Cummings et al., 2011), keeping less energy available for other physiological processes such as growth and reproduction (Wood et al., 2008). The calcification rates in the mussel *Mytilus edulis* and the Pacific oyster *Crassostrea gigas* decreased by 25 and 10%, respectively under an elevated pCO_2 level (740 ppmv) (Gazeau et al., 2007). In addition to impacts on calcification, increased levels of pCO_2, may affect essential physiological processes, such as metabolism and acid-base balance (Shirayama and Thornton, 2005; Munday et al., 2009; Pörtner, 2008; Pörtner and Peck, 2010). In an experiment of acid-base regulation of a benthic sea urchin (*Psammechinus miliaris)*, Miles et al. (2007) showed that sea urchin are unable to compensate acidosis under all CO_2 exposures (pH 6.2–7.4).

Early developmental and life-history stages in benthic invertebrates are excessively susceptible to OA. For example, fertilization rates in echinoderms declined as pCO_2 levels increased from 360 to 10,360 μatm (Kurihara, 2008). The rates of successful cleavage in fertilized eggs of an echinoderm declined by 20% as pH lowerd from 8.1 to 7.7 (Havenhand et al., 2008). Mortality in brittle star larvae increased from 30% at pH 8.1 to 100% at pH 7.9 and 7.7 (Dupont et al., 2008).

Table 1. Summary of the impacts of ocean acidification on some representative benthic invertebrates.

Taxa	Species	pH	CO_2	Impacts	References
Coral	*Acropora palmata*		560 - 800 µatm	52% -73% reduction in recruitment	Albright et al., 2010
	Acropora intermedia		1000–1300 ppm	40 % lower calcification than control	Anthony et al., 2008
	Porites lobata		1000–1300 ppm	Increased 20% bleaching	Anthony et al., 2008
Oyster	*Crassostrea gigas*	7.5	3500 µtm	Increased larval mortality, inhibited shell growth, reduced hardness of shells	Beniash et al., 2010
	Crassostrea virginica		280-800 ppm	16% decrease in shell area and a 42% reduction in calcium carbonate content	Miller et.al., 2009
	Saccostrea glomerata		375- 1000 ppm	64 % reduction in growth rate	Parker et al., 2010
Mussel	*Mytilus edulis*	6.7-8.1		Decreased calcification rate, no growth to reduced growth, 28% smaller than control	Bechmann et al., 2011, Berge et al., 2006, Gazeau et al., 2007
Gastropod	*Thais gradata*	5.8- 8.3		Shell dissolution, decreased aperture length and heavier shell at low pH	Marshall et al., 2008
	Haliotis discus hannai		1650 - 2150 µatm	Fertilization rate and the hatching rate decreased , malformation of shell	Kimura et al., 2011
Clam	*Mercenaria mercenaria*		low aragonite level (<0.3 Ω)	Substantial shell dissolution	Green et al., 2004
Abalone	*Haliotis coccoradiata*	7.6–7.8		Unshelled larvae and abnormal juveniles	Byrne et al., 2011
	Haliotis kamtschatkana		400-1800 ppm	Larval survival decreased by *ca*. 40% in elevated CO_2, larval shell abnormalities in 40% of larvae reared at 800 ppm CO_2, no shell at 1800 ppm	Crim et al, 2011
Crab	*Paralithodes camtschaticus*	7.5		Survival rate decreased ,100% mortality after 95 days but did not affect the calcium carbonate content	Long et al., 2013
	Chionoecetes bairdi	7.5		Survival decreased, 100% mortality after 95 days with reduced calcium carbonate	Long et al., 2013
Sea urchin	*Tripneustes gratilla*	6.6-6.7		Arm length significantly decreased in acidified conditions	Brennand et al., 2010
	Heliocidaris erythrogramma	7.6–7.8		Number of spines decreased with increasing acidification	Byrne, 2011
Brittle star	*Ophiothrix fragilis*	7.7-7.9		30- 100% mortality	Dupont et al., 2008

Metamorphosis, growth, and survivorship of clam, scallop, and oyster larvae all were negatively impacted at 650 ppm pCO_2 compared with controls (Talmage and Gobler, 2009).

To date, there are only few studies investigated the community level responses of benthic invertebrates to OA (Hall-Spencer et al., 2008; Karlen et al., 2010; Kroeker et al., 2011; Hale et al., 2011). Both the mesocosm and *in situ* studies using natural gradient of CO_2 level showed the highest reduction in abundance and diversity in mollusks with response to low pH, whereas annelid abundance and diversity was nearly unaffected by low pH. The arthropod (crustaceans) response was between these two extremes with moderately reduced abundance and diversity at low pH. Kroeker et al. (2011) studied *in situ* benthic communities in three distinct pH zones (6.51 to 8.07 pH) of a CO_2 vents at Ischia island (Italy) and found fewer taxa, reduced taxonomic evenness and lower biomass in extreme low pH area. The impacts of future CO_2 levels on some valuable ecosystems (e.g., Coral) are expected to be rapid (Fig. 3). For example, some models indicate that even if atmospheric CO_2 is become stable at 450 ppm, only 8% of coral reefs will be surrounded by ocean (Cao & Caldeira, 2008). It is projected that if atmospheric CO_2 levels continue to rise as expected, we can expect extinctions of some species by 2050. By 2100, 70% of cold water corals may be exposed to corrosive waters (Cooley et al., 2009). Coral reef damage will also indirectly pressure marine ecosystems by distressing the feeding and reproduction of various reef dependent species (e.g. angel fish, red snapper, damselfish). So, as a result of reduced recruitment, commercially and ecologically important species will be decreased, and ultimately these impaired reefs will have lower biodiversity, will be more susceptible to further injury, and provide fewer ecological services for humans.

Studies on the effects of acidification on benthic food web or ecosystem function are very scant (Hall-Spencer et al., 2008; Kroeker et al., 2011). Kroeker et al., (2011) demonstrated that the trophic structure of an invertebrate community shifted to fewer trophic groups and dominance of opportunistic groups in extreme low pH indicating a simplified food web structure with OA. However, many calcifying benthic invertebrates are positioned at the bottom or middle of the marine food web; consequently, the effects of ocean acidification will be transferred throughout ecosystems (Doney et al., 2009). Almost all commercially harvested fish species prey to some extent on shellfish and crustaceans (larva or adult stage); therefore depletion of calcifying prey would remove or modify traditional food sources and increase competition. For the non-coral reef communities (e.g., estuaries or coastal habitats inhabited by carbonate forming organisms), mechanisms and outcomes of ecosystem modifications are not well studied, but non-coral communities may also undergo similar major changes.

3.2. Interacting effects of multiple stressors

Interests has just grown to focus on the interacting effects of acidification and other climatic stressors on benthic invertebrates (Byrne et al., 2011; Hale et al., 2011) by realizing acidification is only one of several physical changes occurring in marine ecosystems. Temperature, stratification, and hypoxia all are increasing with climate change (Meehl et al., 2007), and all will interact with acidification (Hale et al., 2011). Multiple stressors produce biological responses that are not predictable from single-factor experiments and synergistic interactions have already been observed in response to combinations of elevated pCO_2 and temperature by several studies (Martin and Gattuso, 2009; Brennand et al., 2010; Byrne et al., 2011). For example, larvae of a sea urchin (*Tripneustes gratilla*) reared at pH 7.6 and pH 7.8 had smaller PO arms when compared with those reared at control pH; however, a 3°C increase in temperature diminished the negative effects of low pH/high P_{CO2} (Brennand et al., 2010).They observed the similar PO arm length of larvae reared at 27°C/pH 7.6 and 27°C/pH 7.8 and those reared in control temperature and pH. Byrne et al., (2011) reported that exposure of an abalone (*Haliotis coccoradiata*) and echinoid (*Heliocidaris erythrogramma*) to warming (+2°C to 4°C) and acidification (pH 7.6–7.8) resulted in unshelled larvae and abnormal juveniles, and *Haliotis* development was most sensitive with no interaction between stressors. They found the number of spines for the echinoid decreased with increasing acidification/pCO_2, whereas the interactive effect between stressors indicated that a +2°C warming reduced the negative effects of low pH.

Numerous other key environmental factors will undergo major shifts in the future, including sea surface temperature, water column stratification, and light and nutrient availability; formulating accurate predictions requires considerations for the complex synergistic and antagonistic interactions of all of these many covariables (Hoffmann et al., 2010). So, research into the combined effects of ocean acidification and other human induced environmental changes (e.g., temperature) on marine organisms and food webs is urgently needed.

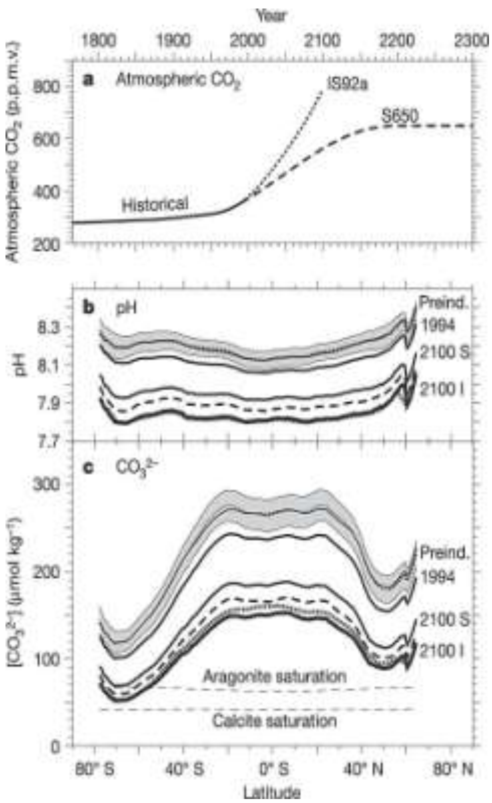

Figure 1. **a**, Atmospheric CO_2 over the industrial period ('Historical') and for two future scenarios: IS92a ('I' in **b** and **c**) and S650 ('S' in **b** and **c**); **b**, Reductions in surface ocean pH due to increases in atmospheric CO_2 ; **c**, Surface ocean [CO_3^{2-}]. (Source: Orr et al., 2005).

3.3. Adaptation and resilience of organisms and ecosystem

Coastal taxa and ecosystem may exhibit variable response to OA, and variation in response to acidification could reflect differences in calcification mechanisms (Ries et al., 2009) and underlying variation in gene code for these responses (Kelly and Hofmann, 2013). Nearly all of the published studies on acidification showed calcifying organisms, including corals, bivalves, gastropods, echinoderms, and crustaceans, are particularly vulnerable. But many species show little to no effect of ocean acidification (Kroker et al., 2010), and others show positive effects (Hendriks et al., 2010). For example, calcification was not reduced for the larvae of the benthic Antarctic sea urchin (*Sterechinus neumayeri*) at low pH (pH 7.0–7.5) waters as compared to skeletal formation in larvae of tropical and temperate sea urchins (Clark et al., 2009). They suggest that *S. neumayeri* may be preadapted to low saturation states and may possess greater mechanistic control over the chemical nature of the extracellular space that surrounds the site of calcification of the larval endoskeleton. This is offering possible evidence for adaptation to changing pCO_2 over geological timescales. So, some organisms may therefore have the capacity to upregulate their metabolism and calcification to compensate for lower availability of carbonate ions.

Variability and stability of marine ecosystems are two important aspects in the context of OA. Some species, in estuaries or in the intertidal zone, are already adapted to live in a variable or fluctuating environment and are therefore relatively flexible in the face of pH variations, whereas other orgamisms that are adapted to live in a more stable environment (e.g., open ocean) are less able to adapt in acidified water (Hofmann et al., 2010). So, because of their long history of exposure to low-alkalinity waters, coastal/estuarine taxa may have greater capacity for adaptation than other marine organisms (Amaral et al., 2011). In addition, physiological tolerance to low pH and carbonate saturation state could already have evolved in response to repeated exposure to such conditions during and preindustrial era and could account for positive responses to acidification reported for some taxa (Gooding et al., 2009; Sanford and Kelly, 2010). Ecophysiological and genotypic studies may provide us an understanding why some species can tolerate a wide range of CO_2 conditions and what process restricts others to the high CO_2 environment.

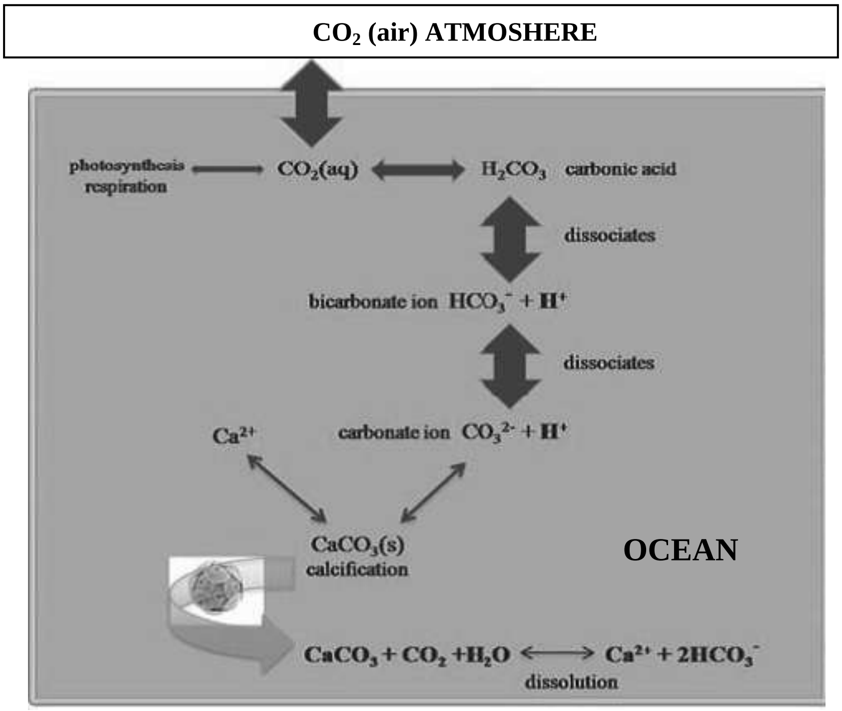

Figure 2. Simplified diagram of the seawater carbonate system. (Modified from Guinotte and Fabry, 2009)

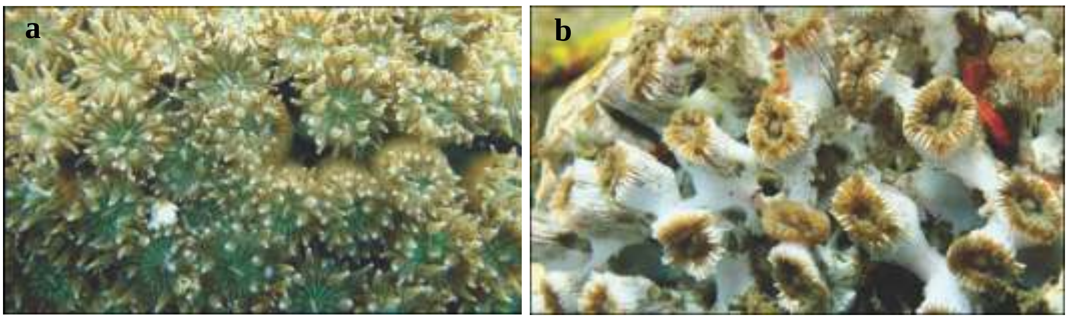

Figure 3. Showing the dissolution of coral after being transplanted for six months into seawater with a pH of 7.8 (a. controls; b. treatment). (Source: Hall-Spencer and Rauer, 2009).

3.4. Methodological approaches used by previous studies

Over the past 10 years a number of different approaches have been undertaken to investigate how increasing ocean acidity can affect marine organisms and ecosystems. The calcification and dissolution of calcium carbonate have been investigated mostly and several approaches have been used to synthesize these information: traditional narrative reviews (Fabry et al., 2008), meta-analyses (Kroeker et al., 2010; Hendricks et al., 2010; Kroeker et al., 2013) and expert surveys. But most studies have investigated the effects of acidification by means of *in vitro* experiments run in small tanks and mesocosms for a short-term using either a defined level of CO_2 or pH and single variable and species (Wernberg et al., 2012). Although mesocosm experiment is a useful tool, variability of the physico-chemical and biological factors that organisms experience in the natural environment can not be included (Wernberg et al., 2012). Moreover, mesocosm experiments can only include a sub-set of species interactions and, consequently, they do not include the complexity of real biological systems (e.g. Sanz-Lazaro et al., 2011). As a consequence, the results obtained from mesocosm experiments conducted in controlled conditions can produce different conclusions to those conducted in more ecologically realistic conditions (Skelly, 2002). Again, the short-term effects do not necessarily predict the long-term ones. For example, Casareto et al. (2009) showed that calcification decreased in coccolithophore *Pleurochrysis carterae* in all CO_2 treatments lasted for short incubations (<39 h), but it increased at high pCO_2 in longer (7-day) experiments.

Field experiments using natural acidity gradients (e.g., CO_2 vents under ocean) has also been used on few occasions to assess the community level effects (Hall-Spencer et al., 2008) and physiological boundaries of calcifying organisms such as corals (Crook et al., 2012) and bryozoans (Rodolfo-Metalpa et al., 2010). These observations at naturally acidified sites provide invaluable information about the ecosystem-level impacts of ocean acidification. Future experiments will need to not only include fixed CO_2 levels, but also a wide range of natural CO_2 variability that is particularly evident in estuaries and upwelling area. Experiments also face challenge in scaling from single-species studies on physiological impacts to ecosystem responses and economic impacts. So, the combination of all of these methods provides convincing evidence for ocean acidification effects at all level, from individual species to ecosystems.

3.5. Future research directions and summary

1. Previous studies show that future OA poses a significant threat to calcifying organisms where most of them are marine benthic invertebrates. Information on less or no calcifying benthic invertebrates (copepods, amphipods, shrimp, polychaetes etc.) is lacking. As these organisms are inseparable part of the benthic ecosystems or food web, future research should include them.
2. The observed biological response of invertebrates to OA at the organism level were varied which might prevent extrapolation at the community and ecosystem level, and possibly lead to confusing decision for the policy makers and coastal managers. Therefore, for improved comprehension of marine ecosystem response to OA needs manipulative experiments on the community level.
3. Field data on ecosystem level effects are lacking. Investigation using natural acidity gradient (e.g., CO_2 vent) can provide useful information in this regard.
4. Experiments combining multiple stressors (temperature, hypercapnia, hypoxia, nutrients) have just been initiated. So further research in multi-stressor and multispecies environment will enable us improving the broader understanding of biological effects of OA on marine benthic invertebrates and more informed adaptation of management and conservation strategies.
5. Studies related to acclimatization, adaptation and evolution are seriously lacking. Invertebrate taxa which are preadapted to fluctuating environment (e.g. coastal and estuarine taxa) may be unaffected and adapt with changing ecosystem. Future studies should include how organisms are adapting to the

variable environment. Ecophysiological and genotypic studies may provide us an understanding why some species can tolerate a wide range of CO_2 conditions and what process restricts others to the high CO_2 environment.

6. Although polar and tropical organisms are likely to be more vulnerable, earlier studies mainly focused on temperate species from North America, Europe and Australia. As polar and tropical organisms living in comparatively more stable environment, future acidification studies should emphasize on them.

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