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Review

The positive relationship between ocean acidification and pollution

Xiangfeng Zeng [a,b], Xijuan Chen [a], Jie Zhuang [a,c,*]

[a] Key Laboratory of Pollution Ecology and Environmental Engineering, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China
[b] University of Chinese Academy of Sciences, Beijing 100039, China
[c] Department of Biosystems Engineering and Soil Science, The University of Tennessee, Knoxville, TN 37996, USA

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ABSTRACT

Ocean acidification and pollution coexist to exert combined effects on the functions and services of marine ecosystems. Ocean acidification can increase the biotoxicity of heavy metals by altering their speciation and bioavailability. Marine pollutants, such as heavy metals and oils, could decrease the photosynthesis rate and increase the respiration rate of marine organisms as a result of biotoxicity and eutrophication, facilitating ocean acidification to varying degrees. Here we review the complex interactions between ocean acidification and pollution in the context of linkage of multiple stressors to marine ecosystems. The synthesized information shows that pollution-affected respiration acidifies coastal oceans more than the uptake of anthropogenic carbon dioxide. Coastal regions are more vulnerable to the negative impact of ocean acidification due to large influxes of pollutants from terrestrial ecosystems. Ocean acidification and pollution facilitate each other, and thus coastal environmental protection from pollution has a large potential for mitigating acidification risk.

Contents

1. Introduction

Increasing atmospheric CO_2 concentrations cause a net air-to-sea flux of excess CO_2, leading to predictable changes in the biogeochemical cycles of many elements and the chemistry of seawater. Changes include increases in the partial pressure of CO_2 (pCO_2), decreases in pH, and decreases in the carbonate concentration $\left[CO_3^{2-}\right]$. This net flux process, known as ocean acidification, is often referred to as "the other CO_2 problem" (Doney et al., 2009). Relative to preindustrial levels, contemporary surface ocean pH has dropped, on average, by about 0.1 pH units (a 26% increase in $[H^+]$). A further decline of 0.2–0.3 pH units will occur over the 21st century unless human CO_2 emissions are curtailed substantially (Orr et al., 2005). Ocean acidification could significantly influence marine ecosystems (Gattuso and Hansson, 2011). One well-known effect is the lowering of the calcium carbonate saturation state, which impacts shell-forming marine organisms,

* Corresponding author at: Department of Biosystems Engineering and Soil Science, The University of Tennessee, Knoxville, TN 37996, USA. Tel.: +1 (865) 974 1325.
E-mail address: jzhuang@utk.edu (J. Zhuang).

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from plankton to benthic mollusks, echinoderms, and coral (Hughes et al., 2003; Hoegh-Guldberg et al., 2007; Pandolfi et al., 2011). Ocean acidification alters phytoplankton abundance and carbon fixation rates in some photosynthetic organisms (both calcifying and non-calcifying) (Doney et al., 2009). For instance, many calcifying species exhibit reduced calcification and growth rates in laboratory experiments under high-CO_2 conditions (Feely et al., 2010). Since photosynthesis is the major consuming process of carbon dioxide, any change in phytoplankton abundance could exert a feedback effect on the overall carbon dioxide balance between the atmosphere and the ocean (Nikinmaa, 2013).

Acidification-induced changes in the attributes of marine ecosystems do not occur in isolation. Non-CO_2 anthropogenic inputs (e.g., pollution) also contribute significantly to the overall acidification threat in some coastal regions (Feely et al., 2010; Cai et al., 2011). Human fossil fuel combustion, fertilizer use, and industrial activity cause a continuous influx of pollutants (e.g., heavy metals, oil hydrocarbons, persistent organic pollutants, pesticides, and eutrophication nutrient elements) into marine ecosystems (Fig. 1). Heavy metals, such as mercury (Hg) and lead (Pb), are the most common types of coastal contaminants detected in relatively high concentrations in waters and sediments of many coastal and estuarine systems (Doney et al., 2009). They can bioaccumulate in the fatty tissues of marine organisms and pass up the food chain to threaten human health through the consumption of contaminated food products, including predatory fish, marine mammals, and seabirds (Elliott and Elliott, 2013; Mostofa et al., 2013). As for oil hydrocarbons, natural seepage alone introduces about 6×10^5 metric tons of crude oil to oceans every year, representing ~47% of all crude oil entering the marine environment. The remaining 53% of crude oil contamination results from anthropogenic activities (e.g., accidental oil spills and transport activities) (Kvenvolden and Cooper, 2003). Exploration of geological phosphate reserves for fertilizer production creates a largely one-way flow of phosphorus from rocks to farms and then to oceans, dramatically increasing eutrophication (Fig. 1). Globally, oxygen-depleted marine coastal "dead zones" caused by eutrophication continue to expand (Diaz and Rosenberg, 2008; Bennett and Elser, 2011). The Gulf of Mexico's "dead zone," averaging more than 17,000 square kilometers in recent years, is forecast to continuously increase (Bennett and Elser, 2011; Slomp, 2011).

Considering the coexistence of ocean acidification and pollution in many coastal regions, these two processes may have combined effects on marine ecosystems in the foreseeable future. Changes in the speciation of heavy metals with water pH could affect the bioavailability and toxicity of those metals (Diaz and Rosenberg, 2008; Millero, 2009). Meanwhile, heavy metals could also influence the rates of photosynthesis and respiration, causing changes in the levels of carbon dioxide and oxygen in seawater. Therefore, when evaluating the impacts of ocean acidification on marine ecosystems, changes in the bioavailability and toxicity of pollutants with changes in pH and oxygenation must be considered. This review aims to summarize relevant information for an insightful analysis of the interactions between ocean acidification and pollution in relation to other stressors to marine ecosystems.

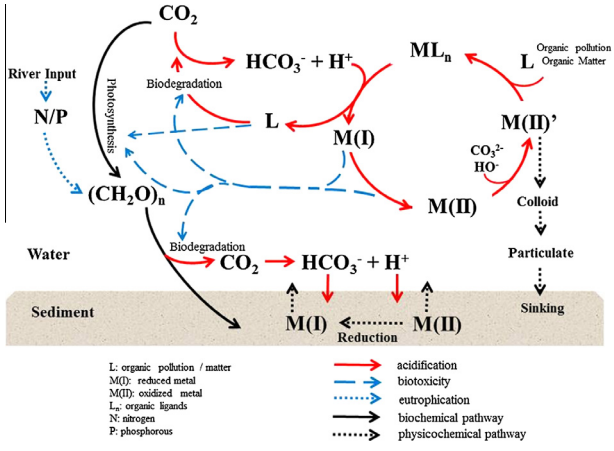

Fig. 1. Interactions between ocean acidification (red) and pollution (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Pollution-facilitated ocean acidification

2.1. Pollutants decrease anthropogenic CO_2 uptake by marine organisms

The effect of pollutants on the abundance of photosynthetic organisms (in comparison to heterotrophs) and their photosynthesis could eventually change the role of ocean autotrophs in global carbon dioxide dynamics as carbon dioxide sinks (Macdonald et al., 2005; Nikinmaa, 2013). Pollutants generally decrease the rate of photosynthesis and in turn CO_2 uptake by ocean phytoplankton (Fig. 1). As an indirect result, the amount of atmospheric CO_2 increases and becomes available for absorption by seawater to enhance acidification. The presence of heavy metals in oceans may inhibit primary production in marine ecosystems and decrease the efficiency of carbon dioxide removal from the atmosphere. Most previous studies have been performed in laboratory cultures (see Table 1). For instance, after 48 h of exposure to 0.031 mg/L of Cu^{2+} for *Microcystis aeruginosa* (*M. aeruginosa*) and 0.047 mg/L of Cu(II) for *Chlorella vulgaris* (*C. vulgaris*), the percentage of cell autofluorescencing decreased, while 0.064 mg/L of Cu(II) decreased both photosynthesis rates and growth rates by 50% (Hadjoudja et al., 2009). Exposure to 50 mg/L and 80 mg/L of Pb(II) for 120 h significantly inhibited the contents of Chlorophyll *a* (chl *a*) in *Chlorella protothecoides* (*C. protothecoides*) by 65% and 49%, respectively (Xiong et al., 2013). When the concentrations of Cd(II) exceed 2.02×10^{-4} mg/L and 3.60×10^{-4} mg/L, the growth of *Thalassiosira pseudonana* (*T. pseudonana*), *Prorocentrum minimum* (*P. minimum*), and *Chlorella autotrophica* (*C. autotrophica*) was significantly slower (Wang and Wang, 2009). At 0.03 mg/L of Hg(II), the growth rate of *C. autotrophica*, *Isochrysis galbana* (*I. galbana*), and *Thalassiosira weissflogii* (*T. weissflogii*) decreased significantly ($p < 0.05$), with calculated LC50 values 0.05 mg/L, 0.09 mg/L, and >0.10 mg/L, respectively (Wu and Wang, 2011; Wu and Wang, 2014). These studies are partially comparable because of the use of a few of the same species and standards in laboratory setups. However, due to the higher concentrations used in the experiments than would be found in natural seawater, bioavailability and biotoxicity of the above heavy metals might be underestimated relative to natural scenarios. Debelius et al. (2011) exposed *Synechococcus* Populations, which were collected from different geographic sites and depths in the Strait of Gibraltar, to solutions of Cu, Ni, and Zn and found that the EC50 value of Cu was as low as $(4.4 \pm 0.4) \times 10^{-3}$ mg/L for surface Atlantic water populations and as low as $(5.9 \pm 0.9) \times 10^{-4}$ mg/L for surface Mediterranean water populations. The LC50s varied from 0.23 mg/L (Atlantic *Prochlorococcus*) to 498.7 mg/L (Black Sea picoeukaryotes) for Cd and from 20.02 mg/L (Mediterranean *Synechococcus*) to 465.2 mg/L (Black Sea nanoplankton) for Pb (Echeveste et al., 2012). For chl *a*, the LC50 of Cd varied from 0.81 mg/L in the Atlantic Ocean to 560 mg/L in the Black Sea, while the LC50s of Pb were much greater, 3080 mg/L and 9240 mg/L, for the Black Sea and Atlantic Ocean experiments, respectively. These results indicate a higher toxicity of Cd than Pb to phytoplankton grown in those seawaters

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