Journal of Experimental Marine Biology and Ecology 475 (2016) 144–153

Contents lists available at ScienceDirect

Journal of Experimental Marine Biology and Ecology

journal homepage: www.elsevier.com/locate/jembe

A decline in macro-algae species resulting in the overwhelming prevalence of *Corallina* species is caused by low-pH seawater induced by short-term acid rain

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ARTICLE INFO

Article history:
Received 24 June 2015
Received in revised form 18 October 2015
Accepted 30 November 2015
Available online 11 December 2015

Keywords:
CO_2
Acid rain
Coralline algae
Intertidal zone
Ocean acidification
Photosynthesis

ABSTRACT

The increase in atmospheric CO_2 and acid rain precipitation are serious global environmental problems that have had worldwide consequences, including the damage of biodiversity in intertidal zones. The decline in species richness in the intertidal zone of Wenzhou, China, is a typical example. In this study, we investigated the effects of CO_2-enriched seawater, CO_2-enriched air and acid rain on a dominant species, *Corallina* sp., and an inferior species, *Ulva conglobata*, in the intertidal zone of Wenzhou. The responses of *Corallina* sp. and *U. conglobata* to high-CO_2 seawater are similar, demonstrating that both of them are tolerant of seawater acidification induced by aerating CO_2-enriched air. The PSII activities of *Corallina* sp. declined markedly when exposed to CO_2-free air, while they increased significantly with high-CO_2 air. An increase of non-photochemical quenching (NPQ) was induced by CO_2-free air, but it declined remarkably with CO_2-enriched air, suggesting that *Corallina* sp. can use atmospheric CO_2 as carbon source for photosynthesis. *Corallina* sp. survived extremely low pH conditions (pH 3) and could regulate the pH of their ambient seawater through the dissolution of $CaCO_3$, while the photosynthetic properties of *U. conglobata* decreased drastically and even the thalli were damaged irreversibly under low pH conditions (pH 3). These results suggest that *Corallina* sp. is much more tolerant of extremely low pH than *U. conglobata*. Based on these results, we suggest that it is not the increase of atmospheric CO_2 but acid rain at least in part contributed to the damage of the biodiversity in the intertidal zone, with the result that these areas are now mainly dominated by *Corallina* sp.

1. Introduction

Since the industrial revolution, human fossil fuel combustion has significantly driven the rapid rise in atmospheric CO_2, the levels of which have increased markedly from approximately 280 parts per million (p.p.m.) to nearly 400 p.p.m. in 2013 (Myers et al., 2014). It is known that the increase in atmospheric CO_2 level has profoundly affected global climate, with effects including global warming and rising sea levels (Orr et al., 2005). In fact, nearly a third of anthropogenic CO_2 released into the atmosphere is absorbed by the ocean (Sabine et al., 2004). The increase in global CO_2 level has also caused a decline in sea-surface pH (Doney et al., 2007, 2009; Orr et al., 2005). In addition, the combustion of fossil fuel has released a huge amount of sulfur dioxide and nitrogen oxide, which can react with the water molecules in the atmosphere to produce acid rain. Widespread acid rain is a well-known worldwide environmental issue, especially in southern China (Larssen et al., 2006). The acid rain in Wenzhou is very serious; the range of pH for acid rain is 3.24 to 6.56 (Zheng, 2012).

Many studies have reported that the increase in both atmospheric CO_2 and acid rain have affected terrestrial plants considerably (Ainsworth and Long, 2005; Drake et al., 1997; Likens et al., 1996; Long et al., 2004; Wang et al., 2013). Elevated atmospheric CO_2 can stimulate higher rates of photosynthesis and increase light-use efficiency in higher plants (Drake et al., 1997; Long et al., 2004), while acid rain can directly damage higher plant leaves, leading to necrosis and chlorosis (Haines et al., 1980; Kováčik et al., 2011; Liu et al., 2011b). Over the past few decades, dieback of the upper canopy caused by acid rain which can be very acidic, with pH values of ~4 has occurred widely in southern China, which has exacerbated the decrease in forest area (Larssen et al., 2006; Liu et al., 2011a). In addition, it has been reported

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http://dx.doi.org/10.1016/j.jembe.2015.11.019
0022-0981/

that the increase in atmospheric CO_2 concentrations can promote marine phytoplankton productivity (Schippers et al., 2004). The enhancement of marine phytoplankton production by nitrogen-enriched acid rain has been reported (Paerl, 1985). Moreover, a few studies have reported the responses including photosynthesis, growth and biomass of several marine macro-algae to ocean acidification (Chen et al., 2014; Gao and Zheng, 2010; Gao et al., 2012; Israel and Hophy, 2002; Martin and Gattouso, 2009). However, to date, the responses of intertidal macro-algae to the increase in atmospheric CO_2 and acid rain remain largely unknown.

The intertidal zone is a special place; a variety of intertidal macro-algae are periodically submerged in seawater at high tide and exposed to air at low tide. During exposure to air, the carbon source of these algae changes from bicarbonate (HCO_3^-) to CO_2 and some intertial macro-algae can benefit from atmospheric CO_2, especially when they dehydrated moderately (Gao and Aruga, 1987; Gao et al., 1999; Maberly, 1990; Maberly et al., 1992; Johnston et al., 1992). As already mentioned, acid rain is a serious worldwide environmental problem. Therefore, during exposure to air at low tide, the intertidal macro-algae are frequently and directly subjected to acid rain stress that often lasts several hours and is very acidic with pH values of 3.24 to 6.56 (Zheng, 2012). Moreover, it has been reported that coralline algal turfs are a dominant characteristic of subtropical and temperate rocky shores (Brown and Taylor, 1999; Steneck et al., 1991). Over the past few years, the biodiversity of the intertidal zones along the coast of Wenzhou, Zhejiang province, China (27°03′–28°36′ N, 119°37′–121°18′ E), has been seriously damaged (Zheng et al., 2011); while most algae population reduced and even disappeared in Nanji Islands, Wenzhou, five coralline algae namely *Corallina officinalis*, *Corallina Pilulifera*, *Amphiroa anceps*, *Amphiroa ephedraea* and *Lithophyllum okamurae*, grew prolifically (Fig. 1) (Sun et al., 2010; Tang et al., 2014). Therefore, the question is whether this phenomenon in the intertidal zone is related to the increase in atmospheric CO_2 and/or acid rain.

Based on the above question, we chose a dominant species, *Corallina* sp., and an inferior species (limited in abundance), *Ulva conglobata*, in the intertidal zone of Wenzhou to analyze the short-term responses of photosynthesis in the two macro-algae to seawater acidification which was induced by aerating CO_2-enriched air and the effects of photosynthesis under enriched atmospheric CO_2. Attention was also paid to the responses and tolerances of the photosynthetic properties of the two macro-algae to low-pH water induced by short-term acid rain.

2. Materials and methods

2.1. Sample collection

Corallina sp. (possible species name is *Corallina officinalis*) and *U. conglobata* were collected from the intertidal zones of Naji island, Wenzhou, China (27°29′ N, 121°05′ E), between May and July 2014. The pH and temperature of seawater at the collecting site is 7.8–7.9 and 18–20 °C, respectively. Healthy thalli in similar morphological and physiological condition were rinsed carefully in sterile seawater to remove visible epiphytes and then cultured for several hours in the laboratory at 20 °C and under a 12 h light:12 h

Fig. 1. (A, B) The crustose *Corallina* sp. in the intertidal zone of Wenzhou, Zhejiang Province, during low tides. (C) *Corallina* sp. collected from the intertidal zones of Wenzhou. The scale bar represents 1 cm.