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Ocean acidification: One potential driver of phosphorus eutrophication

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ABSTRACT

Harmful algal blooms which may be limited by phosphorus outbreak increases currently and ocean acidification worsens presently, which implies that ocean acidification might lead to phosphorus eutrophication. To verify the hypothesis, oxic sediments were exposed to seawater with different pH 30 days. If pH was 8.1 and 7.7, the total phosphorus (TP) content in sediments was 1.52 ± 0.50 and 1.29 ± 0.40 mg/g. The inorganic phosphorus (IP) content in sediments exposed to seawater with pH 8.1 and 7.7 was 1.39 ± 0.10 and 1.06 ± 0.20 mg/g, respectively. The exchangeable phosphorus (Ex-P) content in sediments was 4.40 ± 0.45 and 2.82 ± 0.15 μg/g, if seawater pH was 8.1 and 7.7. Ex-P and IP contents in oxic sediments were reduced by ocean acidification significantly ($p < 5\%$). The reduced phosphorus in sediments diffused into water, which implied that ocean acidification was one potential facilitator of phosphorus eutrophication in oxic conditions.

1. Introduction

Nutrients eutrophication is one dominant promotive factor for harmful algal blooms outbreak which results in various ecological risks (Hart et al., 2015; Zhang et al., 2015). High concentrations of nutrients may lead to eutrophication (Rothenberger and Calomeni, 2016) and attentions from different interest groups have been focused on nutrient eutrophication (Yan et al., 2016). Phosphorus concentration promotion can result in algae multiplication (Wang et al., 1996). Phosphorus limitation for primary production of marine becomes generally because terrigenous phosphorus discharge has been reduced globally (Chen et al., 2015). Thus, harmful algal blooms may occur with high possibility if phosphate concentration increases and the relationships between phosphorus concentration increase and harmful algal blooms outbreak were confirmed by field experiments (Zhang et al., 2007; Yamaguchi et al., 2008; Cao et al., 2009; Xia et al., 2009; Song et al., 2011b; Wang et al., 2011; Gao et al., 2012; Gao et al., 2014). Phosphorus in water body mainly originates from runoffs, marine organisms excretions and diffusion across sediment-water interface (Hessen et al., 2010; García-Romero et al., 2014; Han et al., 2015), and the phosphorus diffusion flux across sediment-water interface is influenced by water pH values (Ni and Wang, 2015; Gainswin et al., 2006). Ocean acidification refers to a reduction in the pH of the ocean over an extended period, typically decades or longer, which is caused primarily by uptake of carbon dioxide (CO_2) from the atmosphere, but can also be caused by other chemical additions or subtractions from ocean (Field et al., 2011). As increased CO_2 discharge, ocean acidification presented by decreased seawater pH value worsens (Yao et al., 2016). Seawater pH value reduction has been observed recently and widely (Ateweberhan et al., 2013; Jin and Gao, 2016), and harmful algal blooms outbreak frequency increases recently (Keesing et al., 2016; Weisberg et al., 2016). Moreover, field experiments showed that the bottom water had high phosphate concentration if the pH value was low (Cao et al., 2009). Thus, there might be one correlation between ocean acidification and frequent outbreak of harmful algal blooms. Is ocean acidification one potential diver for harmful algal blooms outbreak by increasing phosphate concentrations of water body? The question is related to phosphorus cycle under global climate change and measures to reduce ecological stress caused by ocean acidification. However, there is few data about effects of ocean acidification on increase of phosphate concentration in water body especially in oxic conditions.

Thus, effects of ocean acidification on forms of phosphorous in oxic sediments were measured in the present work to verify the hypothesis that ocean acidification might lead to phosphorus eutrophication in water body by changing forms of phosphorus in oxic sediments. The results may shed light on assessment of ocean acidification on phosphorus cycle and control ecological stress caused by ocean acidification. Moreover, the reasons resulting in harmful algal blooms should be reconsidered.

2. Materials and methods

2.1. Sediment samples

Phosphorus is important for seagrasses which can resist ocean acidification successfully (Fabricius et al., 2011; Koch et al., 2013) and it may be one limited factor for seagrass in water area where phosphorus is

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insufficient. One hypothesis that phosphorus released from sediments promoted by ocean acidification might support the primary production of seagrasses is established accordingly. Thus, sediments in seagrass meadow were used in the present work. *Zostera marina* and surface sediments with depth 20 cm were collected in one eelgrass meadow in Shuangdao Bay (37°28′31″ N, 121°58′12″ E), Weihai, Shandong Province, China. To ensure the sediments were oxic, these sampled sediments were mixed adequately and aerated for one day. Then, they were put into plastic buckets with inside diameter 12 cm and height 22 cm. Moreover, the depth of sediment in these plastic buckets was 20 cm. *Z. marina* was cultured in these plastic buckets and the buried root depth in sediments was 2 cm. Three plastic buckets were put into one plastic box with size 60 × 40 × 35 cm. The coastal water sampled from Shuangdao Bay with salinity 30‰ was put into the box. Moreover, the distance between water and sediment surface was 10 cm. Water flow with speed about 0.27 cm/s was drove by one water circulating pump. Furthermore, the illumination intensity was 4500–5000 Lux andits period was 12 L:12 D. The water temperature with range 10–15 °C varied naturally. The aquatic system including sediments and *Z. marina* was designed to acclimate the indoor conditions for one month, however, it had to be kept for 5 months because of manpower shortage and laboratory reconstruction. After five-month adaptation, sediments in these buckets were poured out and the macro benthos and stones were screened out. Then, these sediments were aerated and mixed fully to determine effects of ocean acidification on forms of phosphorus in oxic sediments.

2.2. Determination of the effects of ocean acidification on the forms of phosphorus in the sediments

Uniform mixed sediments were put into plastic bucket with inside diameter 12 cm and depth 22 cm, which was put into one plastic box with size 60 × 40 × 35 cm. Coastal water with salinity 30‰ sampled from Shuangdao Bay was put into the box. The distance between water and sediment surface was 15 cm. Moreover, the experimental water was filtered by degreasing cotton with water absorption ≥ 23. Water flow with speed about 0.27 cm/s in the boxwas drove by one circulating pump. Moreover, the illumination intensity was 4500–5000 Lux andits period was 12 L:12 D. The water temperature was about 20 °C and it varied naturally. According to the normal seawater pH value and the ocean acidification trend (Riebesell et al., 2010), two pH values were set and they were 8.1 and 7.7, respectively.The normal water pH value is 8.1. Climate models predict additional declines of as much as 0.3–0.4 pH units by the year 2100 (Doney et al., 2012), which means that ocean acidification with pH 7.7 is projected to be observed in the global ocean in 2100. Ocean acidification with pH 7.7 was simulated by CO_2 injection to seawater. The hyperpietic CO_2 got into water through high pressure tank (7 Mpa), pressure relief valve (YQT-3), solenoid valve (TG22-08) and trim switch (SV-02). The CO_2 aeration quantity was controlled by pH control meter (Weipro pH-2010). Moreover, there were three parallels for every treatment.

After exposure to seawater with different pH values 30 days, the surface sediments with depth 6 cm were sampled by PVC pipe with inside diameter 1.5 cm. During the 30 days, the pH 7.7 was maintained by controlling CO_2 aeration quantity. The seawater with pH 8.1 was left untreated and the measured pH was 8.11 ± 0.03 (mean ± standard deviation).

2.3. Analysis of the forms of phosphorus in the sediments

Sediments exposed to seawater with different pHwere dried to constant weight at 65 °C and the dried sediments were grinded slightly to keep the natural grade size. The dried 0.10 g sediments were added into 25 mL oxidant that consisted of $K_2S_2O_8$ (0.15 mol/L) and NaOH (0.15 mol/L). After 1-h nitration at 120 °C and 0.12 Mpa, the mixture was centrifuged at 4000 r/min (3761 g) for 10 min. The supernatant fluid was collected to determine the total phosphorus (TP) content in sediments (mg/g) by the phosphomolybdate blue method (Li et al., 2007).

The dried 0.10 g sediments were added into 25 mL HCl (0.10 mol/L). After 2-h oscillation, the mixture was centrifuged at 4000 r/min (3761 g) for 10 min and the supernatant was collected to determine the phosphorous content in sediments ($P_{un\text{-}burned}$) (mg/g). Moreover, the dried 0.10 g sediments were burned at 450 °C for 5.5 h. Then the ashes were added into 25 mL HCl (0.10 mol/L). After 2-h oscillation, the mixture was centrifuged at 4000 r/min (3761 g) for 10 min and the supernatant was collected to determine the phosphorous content in sediments (P_{burned}) (mg/g). The inorganic phosphorus (IP) content in sediments (mg/g) was calculated by $TP + P_{un\text{-}burned} - P_{burned}$.

The dried 1.00 g sediments were added into 25 mL $MgCl_2$ (1.00 mol/L). After 2-h oscillation, the mixture was centrifuged at 4000 r/min (3761 g) for 10 min. The supernatant fluid was sampled to determine the exchangeable phosphorus (Ex-P) content in sediments (μg/g) by the phosphomolybdate blue method (Zhang et al., 2013).

2.4. Statistical methods

To analyze effects of ocean acidification on forms of phosphorus in sediments, One-way ANOVA was conducted if variances of contents of phosphorus with different forms in sediments were homogeneous, during which the multiple-comparison was conducted by the Bonferroni test. Otherwise, the Dunnett-T3 test was used to compare effects of ocean acidification on forms of phosphorus in sediments. The significant level was 5%.

3. Results

3.1. TP and IP contents in sediments

After exposure to seawater with different pH for 30 days, the TP content in sediments with depth 6 cm reduced as decreased seawater pH value, however, the difference was not significant (Fig.1). The TP content in sediments exposed seawater with pH 8.1 was 1.52 ± 0.50 (mean ± standard deviation) mg/g and that in sediments exposed to ocean acidification with pH 7.7 was 1.29 ± 0.40 mg/g. IP content in sediments

The IP content in sediments with depth 6 cm significantly reduced as decreased seawater pH values after the sediments was exposed to seawater with different pH values for 30 days ($p < 5\%$) (Fig.1). The IP content in oxic sediments exposed to seawater with pH 8.1 was 1.39 ± 0.10 (mean ± standard deviation) mg/g, which was significantly higher than that in sediments exposed to ocean acidification with pH 7.7 (1.06 ± 0.20 mg/g) ($p < 5\%$).

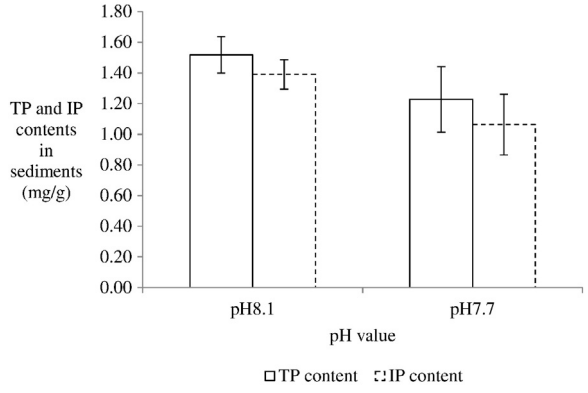

Fig. 1. TP and IP contents in sediments exposed to seawater with different pH values.