

IMPACTS OF MARINE RANCHING CONSTRUCTION ON SEDIMENT PORE WATER CHARACTERISTIC AND NUTRIENT FLUX ACROSS THE SEDIMENT–WATER INTERFACE IN A SUBTROPICAL MARINE RANCHING (ZHELIN BAY, CHINA)

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Abstract. Marine ranching is an effective way to restore depleted stocks and increase fisheries production. The effects of marine ranching construction on sediment pore water characteristics and nutrient flux across the sediment–water interface were determined by incubation experiments. Nine stations were selected along an inshore to offshore gradient of different sediment types representing different zones used for marine ranching in Zhelin Bay, China. The results showed that nutrient concentrations of overlying water and pore water varied by zone and were influenced by biological and physical characteristics. In the macroalgae zone (MA), macroalgae was cultured from September to May. Decayed macroalgae in this zone during winter lead to pH variation (ranged from 8.05 to 8.16) and highest nitrite (range from 0.1719 to 0.9210 $\mu\text{mol m}^{-2} \text{D}^{-1}$), ammonia (range from 1.778 to 4.448 $\mu\text{mol m}^{-2} \text{D}^{-1}$) and total nitrogen (range from 23.43 to 140.6 $\mu\text{mol m}^{-2} \text{D}^{-1}$). In the benthic molluscs' area, shellfish activities led to higher ammonia (range from 0.3312 to 7.725 $\mu\text{mol L}^{-1}$) and total nitrogen (range from 59.67 to 447.7 $\mu\text{mol L}^{-1}$) concentration in the overlying water during the summer season. In the artificial reef zone (depth 15–20 m), the deployment of artificial reef materials altered the sea floor which resulted in upwelling and a consequent increase in the flux of total phosphate. The results of this study will be useful to improve marine ranching efforts in China and worldwide.

Keywords: *fishery, macroalgae, benthic molluscs, artificial reef, water quality*

Introduction

Sustainable fisheries are a useful way to restore depleted stocks and increase production (Bell et al., 2008; Taylor et al., 2016). Stock enhancement and marine ranching have been proven to be an effective method to increase stocks (Camp et al., 2013; Hair et al., 2016; Leber et al., 2004; Lorenzen et al., 2010; Han et al., 2016). In recent years, marine ranching combined with artificial reef deployment has been used on a massive scale in China, Japan and other countries (Leber et al., 2004). A typical marine ranch in China is divided into four functional components including the artificial

reef zone, macroalgae zone, mollusc zone and floating reef zone (Chen et al., 2015) and each zone has different ecological function. The artificial reef zone and floating reef zone provide shelter for fishery resources and enhance water nutrient; shellfish in the mollusc zone feed on microalgae; macroalgae absorb nutrients decrease red tide and provide food for human consumption.

The impacts of marine ranching on the physical, chemical and biological environments in each functional part would be significantly different (Gaertner-Mazouni et al., 2012; Layman et al., 2016; Raoux et al., 2017; Seaman, 2000; Wang et al., 2016; Wu et al., 2016). Thus, it is important to evaluate the biogeochemical changes associated with marine ranching construction. Models of mass fluxes and transformations of nutrients were used to describe the physical and biogeochemical process (Arndt et al., 2009; Denis and Grenz, 2003; Hu and Li, 2009; Miller, 1984; Rasheed et al., 2003). Dominant macrofauna enhanced benthic molecular diffusion and changed the biochemical processes in sediment (Zheng, 2011). Warnken et al. (2003) found shrimp trawling with removal of the upper oxic sediment layers could trend in benthic–pelagic coupling. Layman et al. (2016) proved that artificial reef deployment would enhance the primary production in seagrass ecosystem. Yet this rather general observation leaves many things unexplained about specific mechanistic links between marine ranching construction and nutrient supply.

The aim of this study was to assess nutrient fluxes across sediment–water interface and to evaluate the effects of marine ranching construction - artificial reef deployment, mollusc enhancement and macroalgae culture on sediment biogeochemistry. To help constrain the results, we have chosen a study site where benthic animal and fishery resources have been surveyed previously (Chen et al., 2015).

Materials and methods

Study area and sampling

Zhelin Bay is located in the north of Guangdong Province, China, with an area of 1320 km². It was an important fishing ground of the north South China Sea. However, increased fishing effort in this area has led to a substantial decline in its fishery resources. Thus, to enhance fishery resources the area was selected as a location for constructing a Zhelin marine ranching system (ZSR). There are four parts in ZSR; the artificial reef zone (AR), the benthic molluscs zone (BM), the macroalgae zone (MA) and the floating reef zone (cages) (FR). Sampling sites in ZSR were selected in AR, BM and MA respectively.

Sediment cores were collected at the selected sites by SCUBA in two seasons (summer and winter) in 2012 (*Table 1, Figure 1*).

Table 1. Location of sample sites

Stations	Description	Latitude (North)	Longitude (East)
S		117°00'10.80"	23°32'27.60"
S	Macroalgae cultured area	117°03'32.40"	23°32'27.60"
S		117°06'05.40"	23°30'00.00"
AR		117°10'15.60"	23°31'01.20"
AR	Artificial reef deployed area	117°10'15.60"	23°29'34.80"
AR		117°11'24.00"	23°29'34.80"
M		117°05'60.00"	23°28'13.80"
M	Molluscs enhanced area	117°03'21.00"	23°28'46.80"
M		117°01'17.88"	23°26'56.40"

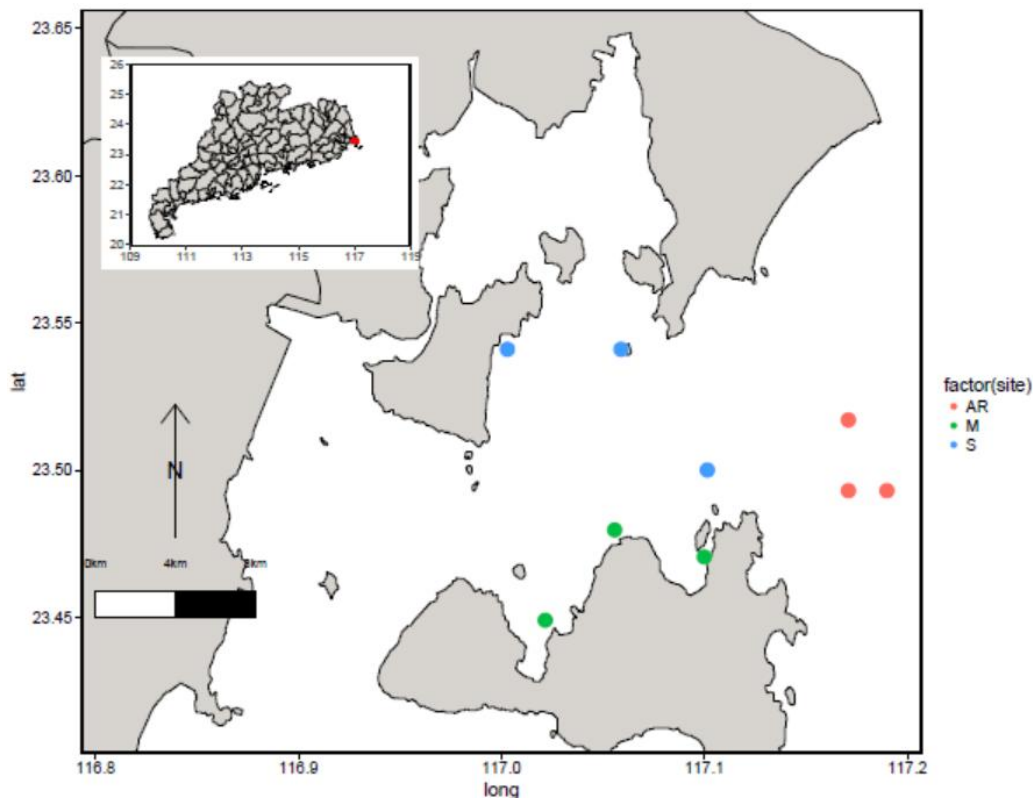


Figure 1. Sample sites in Zhelin Bay marine ranching, China. AR: artificial reef deployed area; M: molluscs enhanced area; S: macroalgae cultured area

Sediment cores of 0-30 cm were collected with stainless steel column sampler (5 cm in diameter). Then, sediment cores were transferred into transparent PVC wetland column without disturbance (30 cm in height and 5 cm in diameter), and immediately frozen ($-20\text{ }^{\circ}\text{C}$) and preserved with HgCl_2 until analysis was performed.

Nutrient incubated fluxes

The incubation device used in this study was designed by Qin et al. (2012) (Fig. 2). Samples were collected as 15 cm-long sediment cores including 15 cm of the overlying water column. Each sediment core was sliced at 2 cm intervals over the first 10 cm with Rhizon to collect pore water (Seeberg-Elverfeldt et al., 2005) (Fig. 3). The temperature of the dark refrigerated cabinets was set at $10\text{ }^{\circ}\text{C}$ and $25\text{ }^{\circ}\text{C}$ to simulate the winter and summer temperature of ZSR, respectively. The overlying water was centrifuged at 50 r/min at AR samples, 40 r/min at BM samples, 30 r/min at MA with a motor rotating propeller which was positioned at the same distance (10 cm) above the sediment surface in all core tubes. The differences of revs among samples of different areas are according to the water current of the areas. All sea water samples were taken from ZSR before each experiment and returned to the lab with $4\text{ }^{\circ}\text{C}$ cabinet. Sampling of the overlying water was done by a plastic outlet at 0 h, 4 h, 8 h, 12 h, 24 h, 36 h, and 48 h and pore water by means of Rhizon at 8 h and 48 h of the incubation period. The water volume removed during sampling was compensated by simultaneous input through the inlet, which retained the physical and chemical properties and total volume in the overlying water.

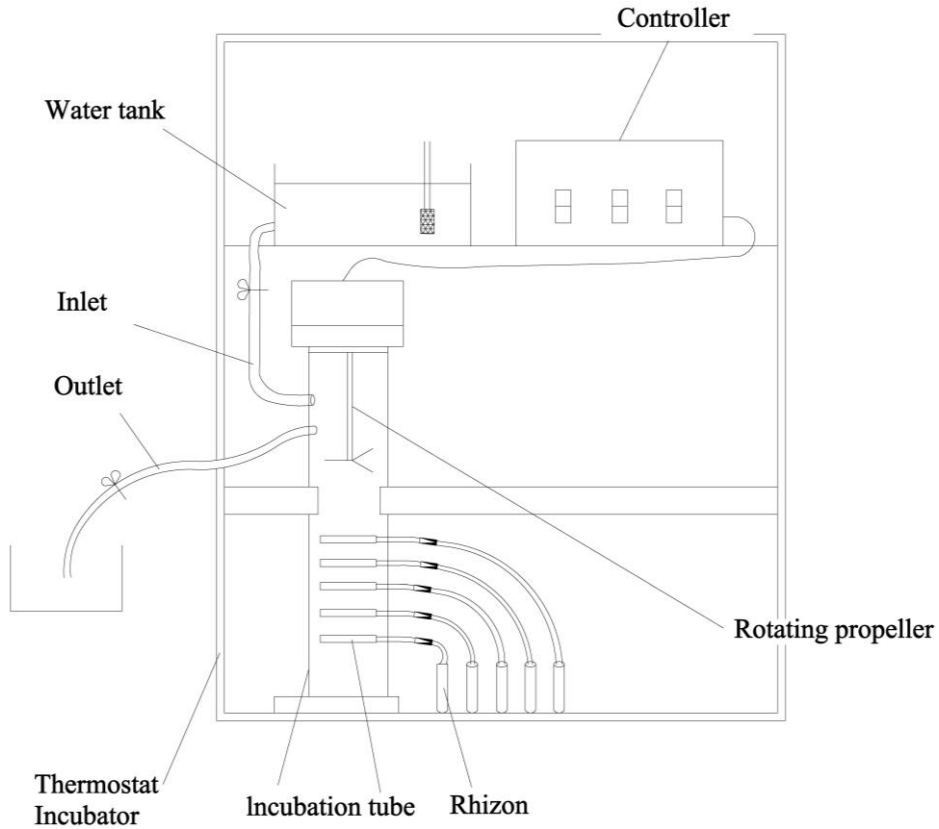


Figure 2. Equipment used for measurements of benthic nutrient fluxes during incubations

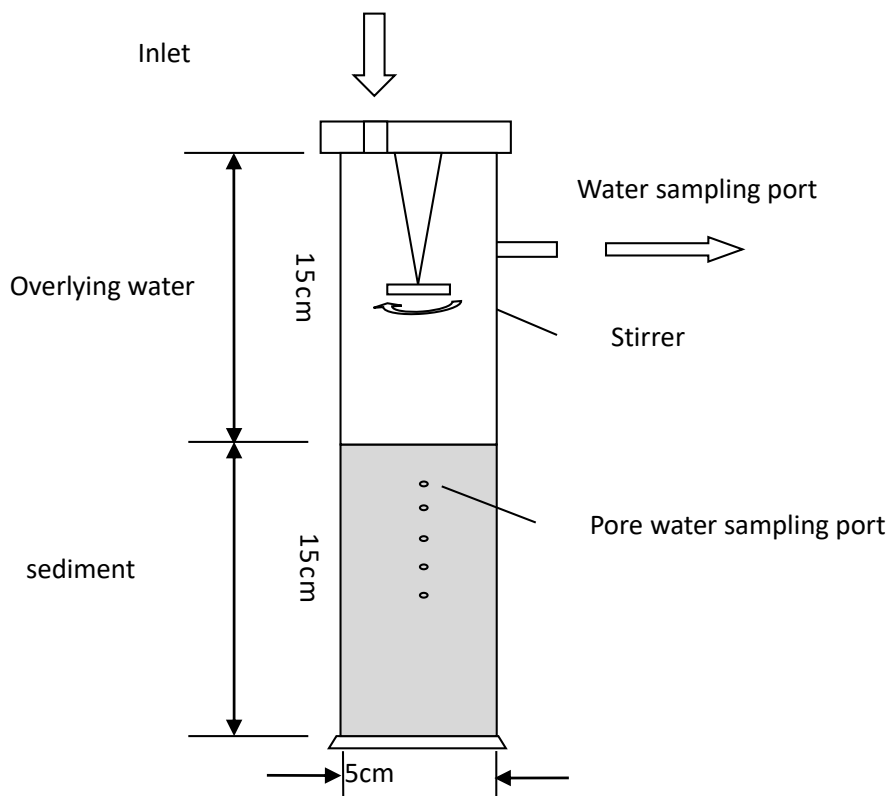


Figure 3. The incubation tube of incubation device

DO and pH of overlying water were analyzed using a hand held YSI (YSI 650, YSI Incorporated). The overlying water and pore water samples were rapidly filtered using Whatman filter paper (Pore 0.45 μm and diameter 47 mm; Whatman Inc., Florham Park, NJ) and analyzed for ammonia (NH_4^+), nitrite (NO_2^-), phosphate (PO_4^{3-}), total nitrogen (TN) and total phosphorus (TP). Concentration of NH_4^+ , NO_2^- , PO_4^{3-} , TN and TP were determined spectrophotometrically using FIAstar5000 nutrient analyzer (FOSS Company) according to the methods described by Grasshoff et al. (2009).

Fluxes calculation and data analysis

The fluxes of NH_4^+ , NO_2^- , PO_4^{3-} , TN and TP across sediment–water interface were calculated according to Fick's 1st law and using the following formula (Eq. 1) (Sakamaki et al., 2006):

$$F = \frac{[(C_s - C_i) - (C'_s - C'_i)]}{(t_i - t_j) \times A} \times V \quad (\text{Eq. 1})$$

where F is the nutrient flux ($\text{mg m}^{-2} \text{h}^{-1}$), C_s and C_i are the nutrient concentration in the overlying water and pore water at the time of t_j , C'_s and C'_i are the nutrient concentration in the overlying water and pore water at the time of t_i , t_j and t_i is the time of beginning of incubation and end of incubation, individually, A is the sediment surface area in incubation tube and V is water volume.

Fluxes between the different pore water were calculated as follows (Eq. 2) (Zhang et al., 2013):

$$F = \frac{(C_s - C_i)}{(t_i - t_j)} \times H \quad (\text{Eq. 2})$$

where H was the height between the different pore.

A series of possible fits are compared through statistical F testing. Fluxes were calculated as slopes of linear regression of the changes in nutrient concentrations against time. Statistical significance of regression analysis was evaluated by a criterion of $p < 0.05$.

Results

Overlying water

DO and pH in the overlying water are illustrated in *Figure 4*. Dissolved oxygen in the overlying water decreased quickly in the first 4 h and then remained at a relatively stable concentration; no obvious differences were found among sites and seasons. The exception was site AR and MA in summer, where lower DO values were measured. Higher depleted rate of DO concentrations in site MA were probably due to decaying macroalgae (Wang et al., 2016). Otherwise, artificial reef construction will affect the local physical dynamics in the small-scale environments (Kim et al., 2016; Seaman, 2000). A large reef structure can create locally significant vertical upwelled current and cause resuspension or scouring of sediment around the reef bottom.

The concentration of NH_4^+ , NO_2^- and PO_4^{3-} was highly variable (*Fig. 5*). Ammonium is higher than nitrite in site BM and MA during the incubated period. The highest

concentration of ammonium was found in summer at site BM ($11.99 \pm 2.01 \text{ } \mu\text{mol L}^{-1}$, after 24 h incubation in summer). At site AR the concentration of ammonium in summer is lower than during winter. However, the trend of nitrite is reversed. At site BM, Nitrite levels are the lowest among all sites, though ammonium level was the highest. Phosphate concentrations were low at sites BM and MA (Fig. 6). Phosphate concentrations revealed no obvious differences among all sites and seasons (summer and winter, $P > 0.05$). Highest phosphate levels were found in winter after a 4 h incubation period at site AR ($5.360 \text{ } \mu\text{mol L}^{-1}$).

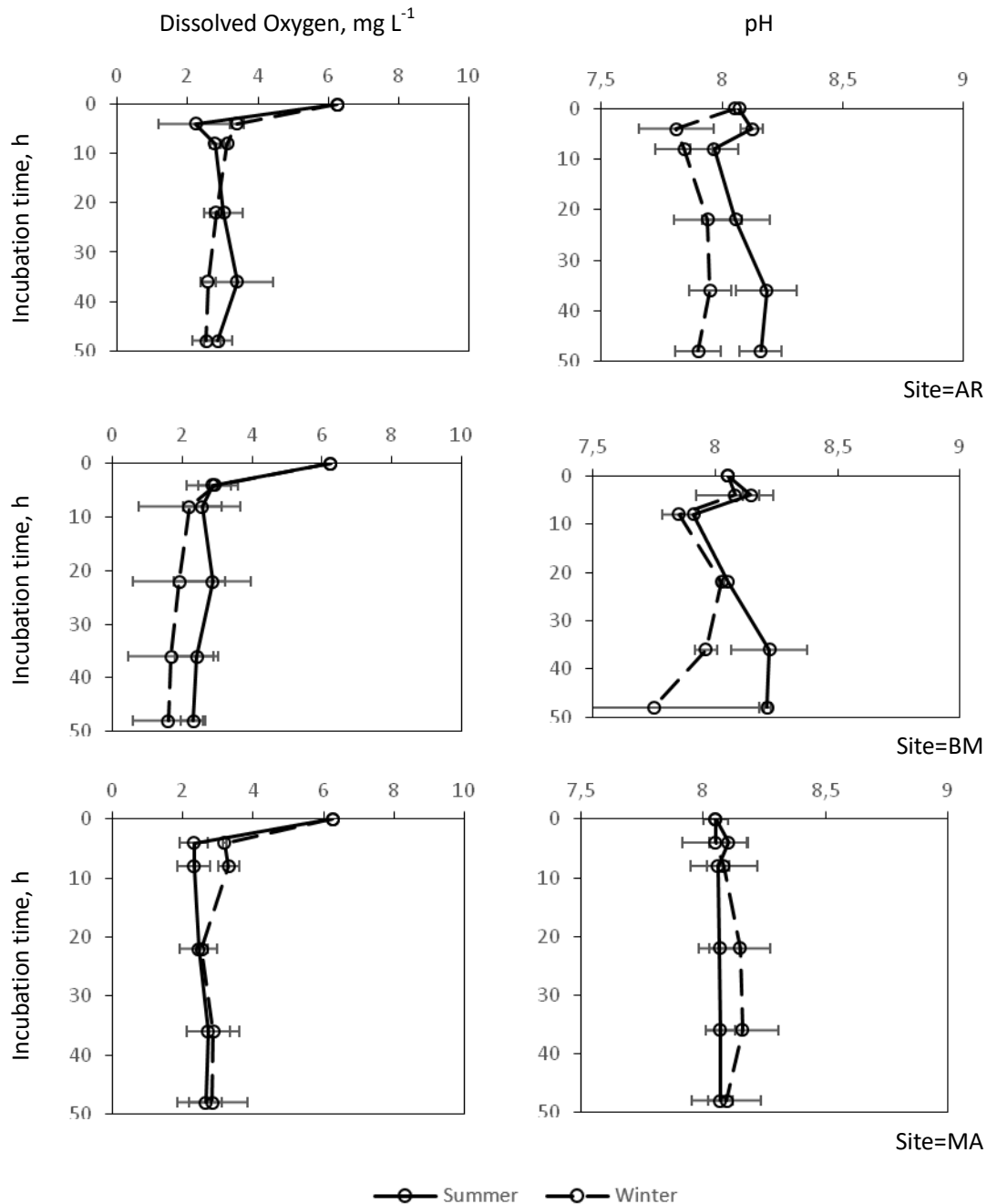


Figure 4. Time course of DO and pH in the overlying water during the incubation in summer and winter

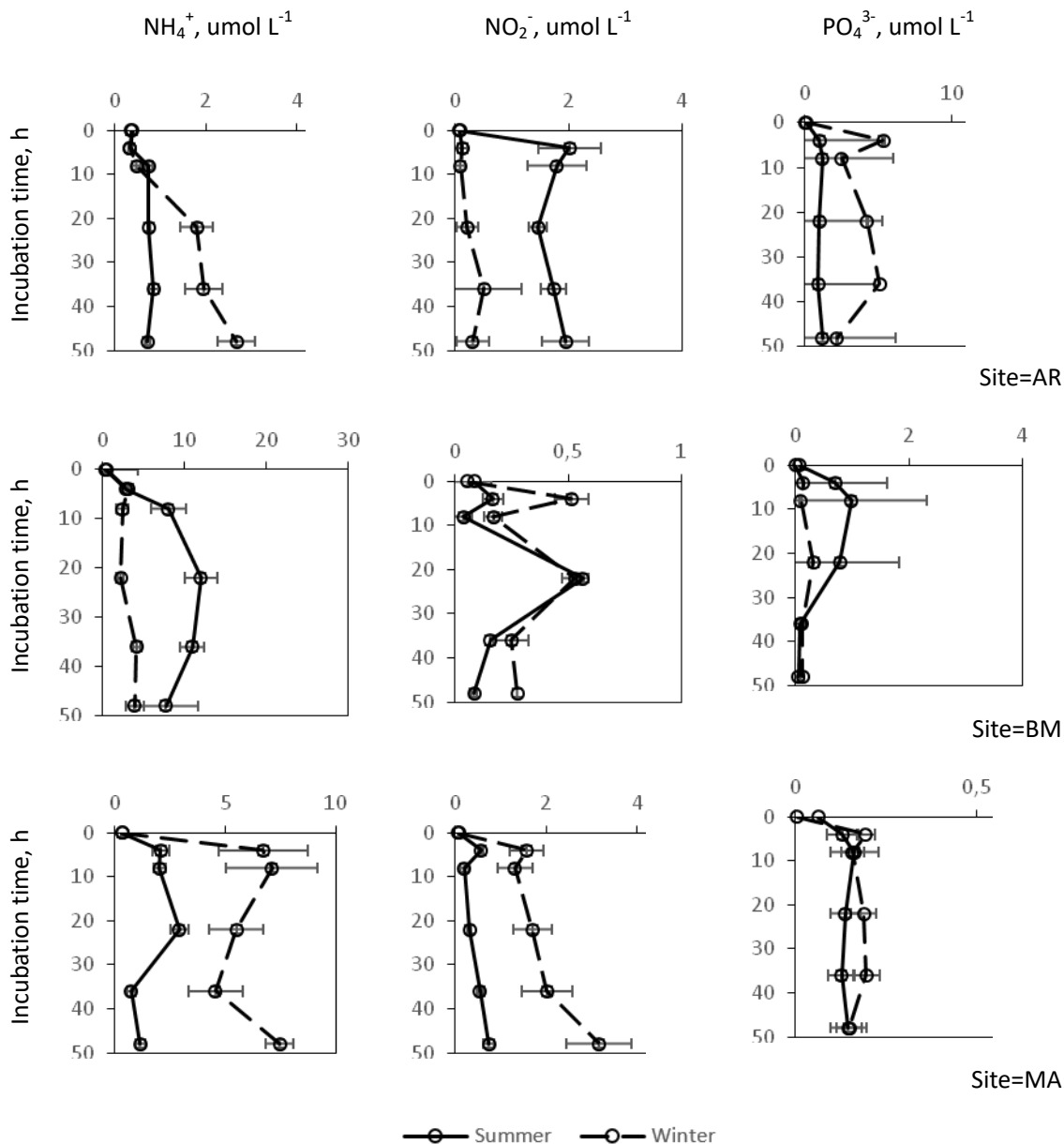


Figure 5. Time course of ammonium, nitrite and phosphate during the incubation in spring and winter

The range of TN and TP concentration in the overlying water throughout the incubation time was about one order of magnitude greater than TN and TP variations observed during the first 4-h incubations (Fig. 5). The TN levels were always higher than TP in both seasons and at all sites. The highest TN concentrations ($447.1 \pm 63.32 \mu\text{mol L}^{-1}$) were found in summer at site BM. After incubation the higher TN concentration were found at site AR in winter ($325.8 \pm 46.83 \mu\text{mol L}^{-1}$) and at site MA in both summer and winter ($328.5 \pm 30.61 \mu\text{mol L}^{-1}$ and $330.3 \pm 50.97 \mu\text{mol L}^{-1}$, respectively). TP concentrations were generally lower in summer and winter at site AR and in winter at site MA. These results mean that the high density of mollusc in site BM had bioturbation effects on benthic biogeochemistry.

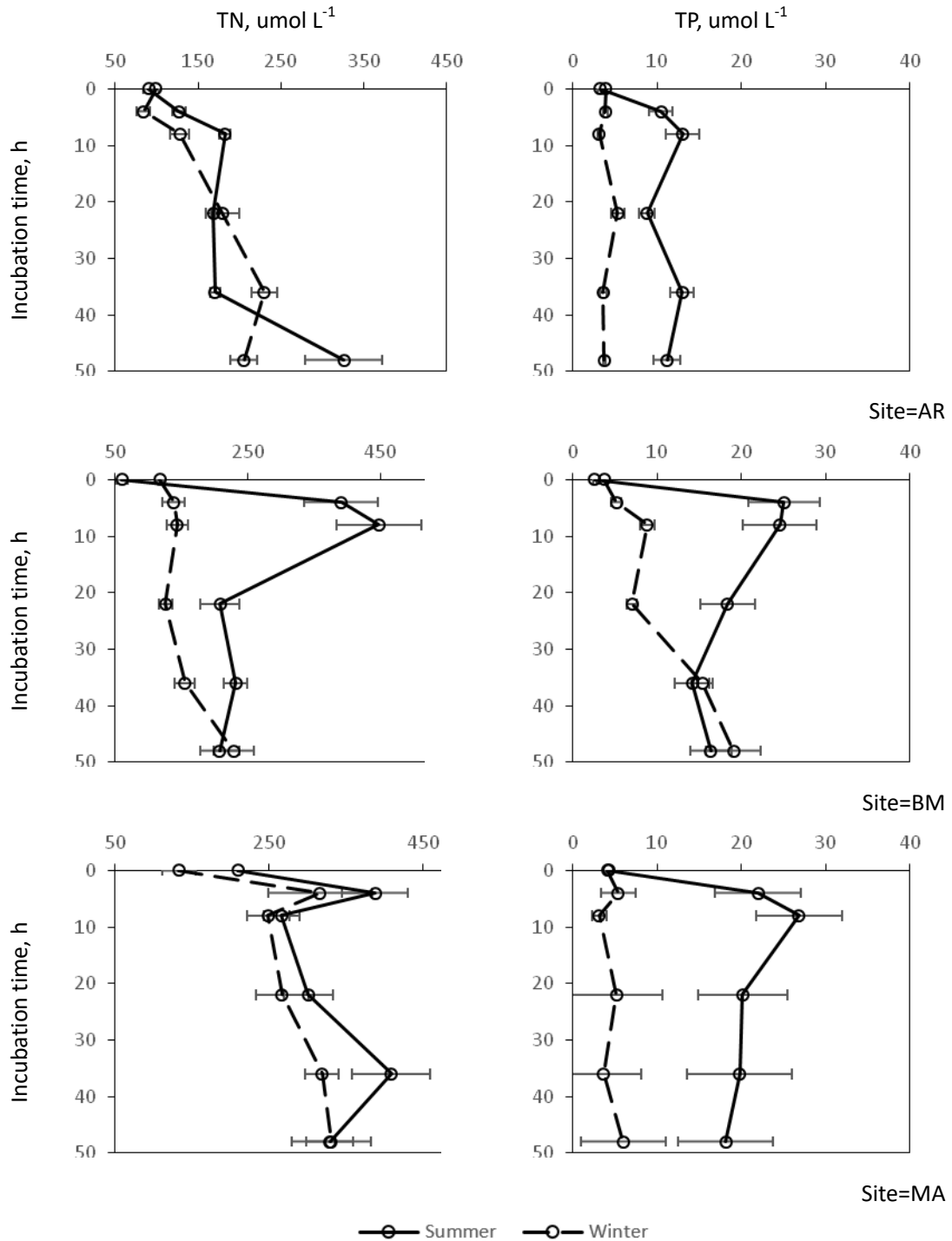


Figure 6. TN and TP in the overlying water in summer and winter

Pore water

For all sites, ammonium, nitrite and phosphate concentrations showed a sharp increase in the first 2 cm depth of the sediment and then demonstrated regular fluctuations with depth (Fig. 7). The pore water ammonium concentrations were approximately similar at both sites BM and MA for both seasons (varying from 2.428 to

55.68 $\mu\text{mol L}^{-1}$ and from 1.996 to 54.03 $\mu\text{mol L}^{-1}$ in sites BM and MA respectively). The highest ammonium concentrations were detected at site AR in winter (77.50 $\mu\text{mol L}^{-1}$). Nitrite concentration showed a similar trend to ammonium, however the highest nitrite concentration 1182.14 $\mu\text{mol L}^{-1}$ was found at site MA in summer after 48 h of incubation. The pore water phosphate concentration showed a gradual increase with depth and no conspicuous difference between the two seasons. However, phosphate concentration at site AR showed higher value than the other sites and with a strong positive gradient in overlying water. Significant variation ($p < 0.05$) of nitrite concentration with seasons were detected only in sites AR and BM. There are no significant differences between 8 h incubation and 48 h of incubation for ammonium, nitrite and phosphate concentrations ($p > 0.05$). TP and TN showed almost similar trend (Fig. 8). Total phosphate concentration at site BM was significantly lower than at site AR and MA (varying from 3.092 to 116.7 $\mu\text{mol L}^{-1}$, from 8.802 to 167.00 $\mu\text{mol L}^{-1}$ and from 3.112 to 187.2 $\mu\text{mol L}^{-1}$ in site BM, AR and MA respectively).

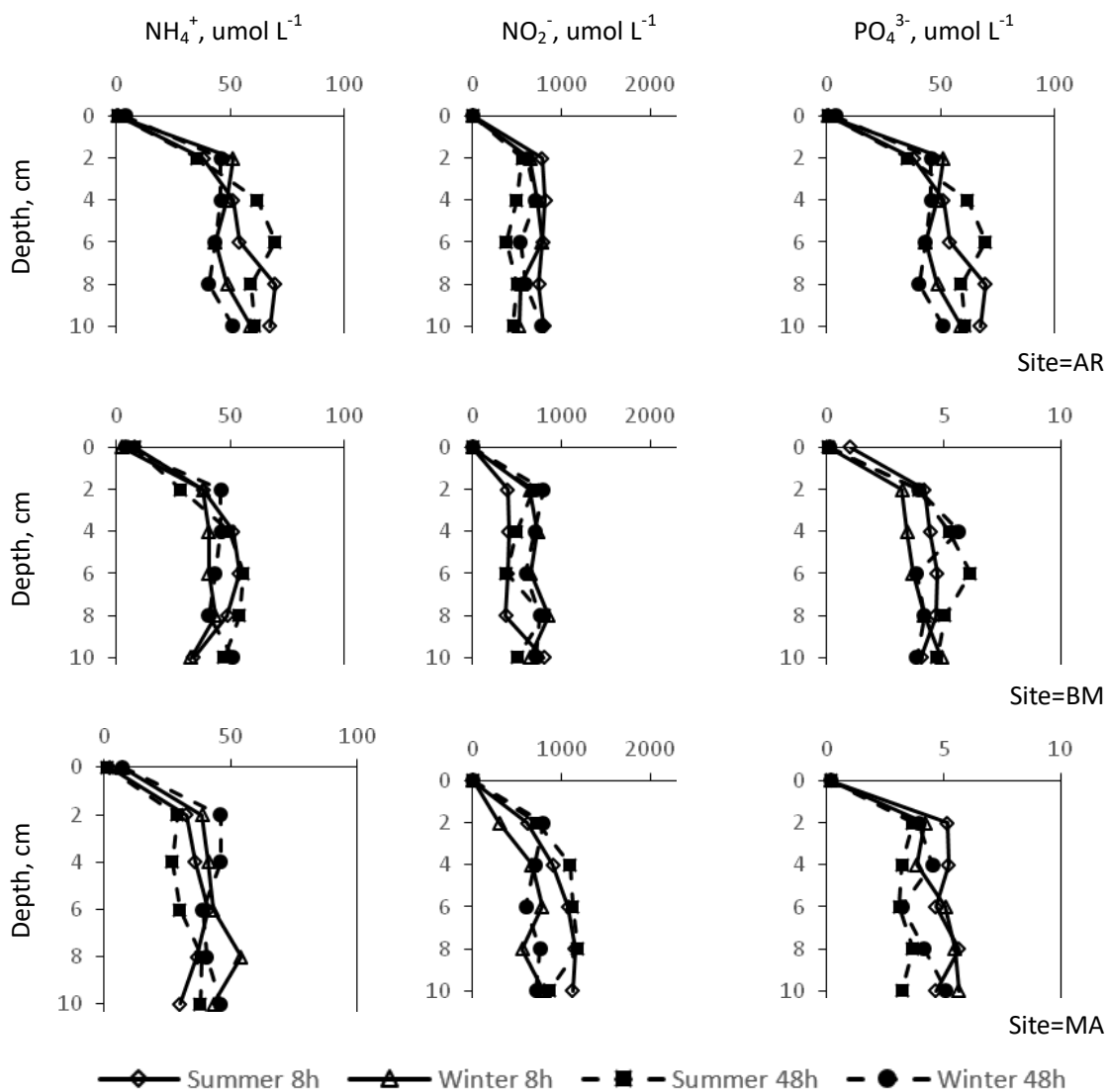


Figure 7. Ammonium, nitrite and phosphate in the pore water after 8 and 48 h of incubation for spring and winter

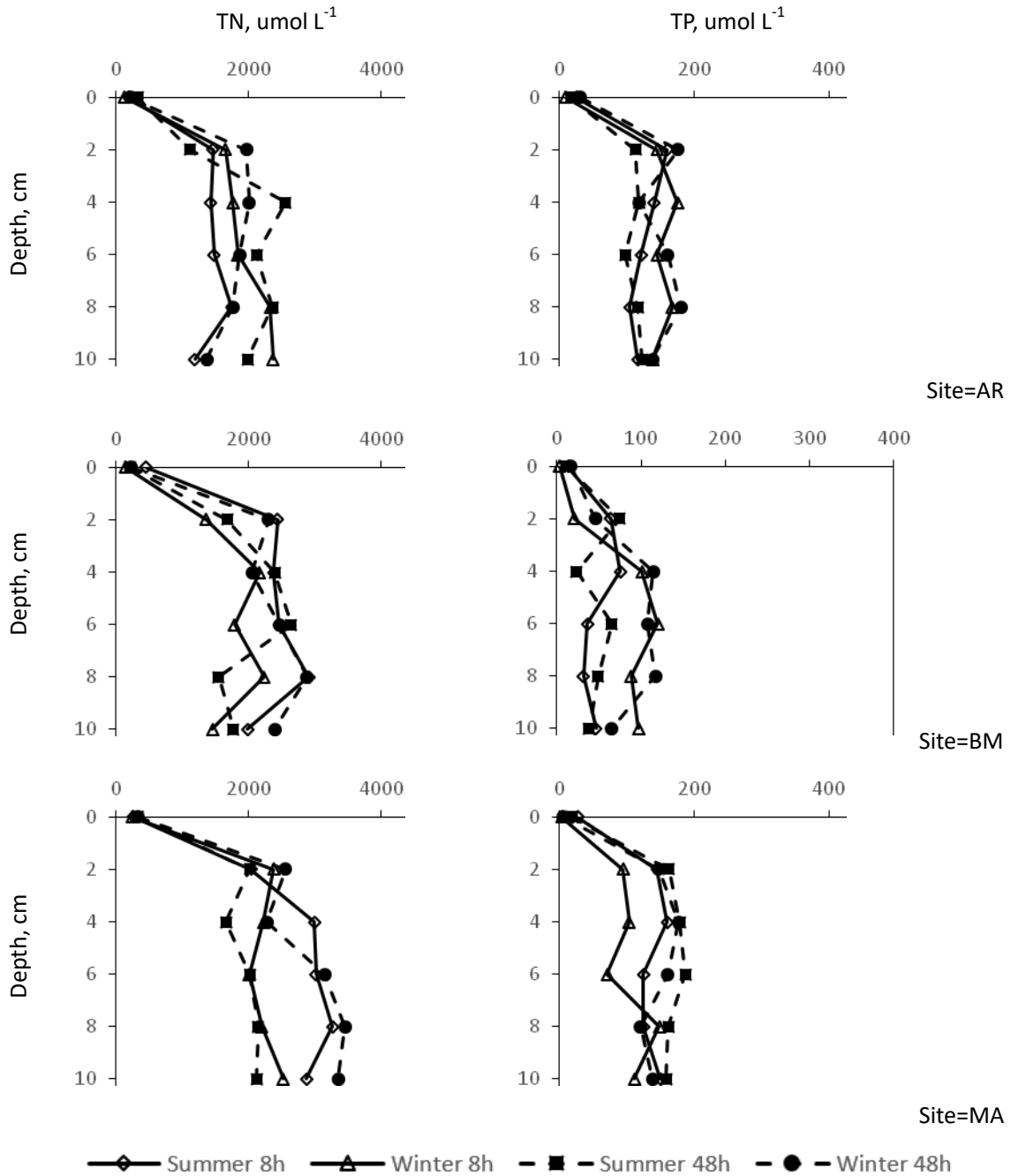
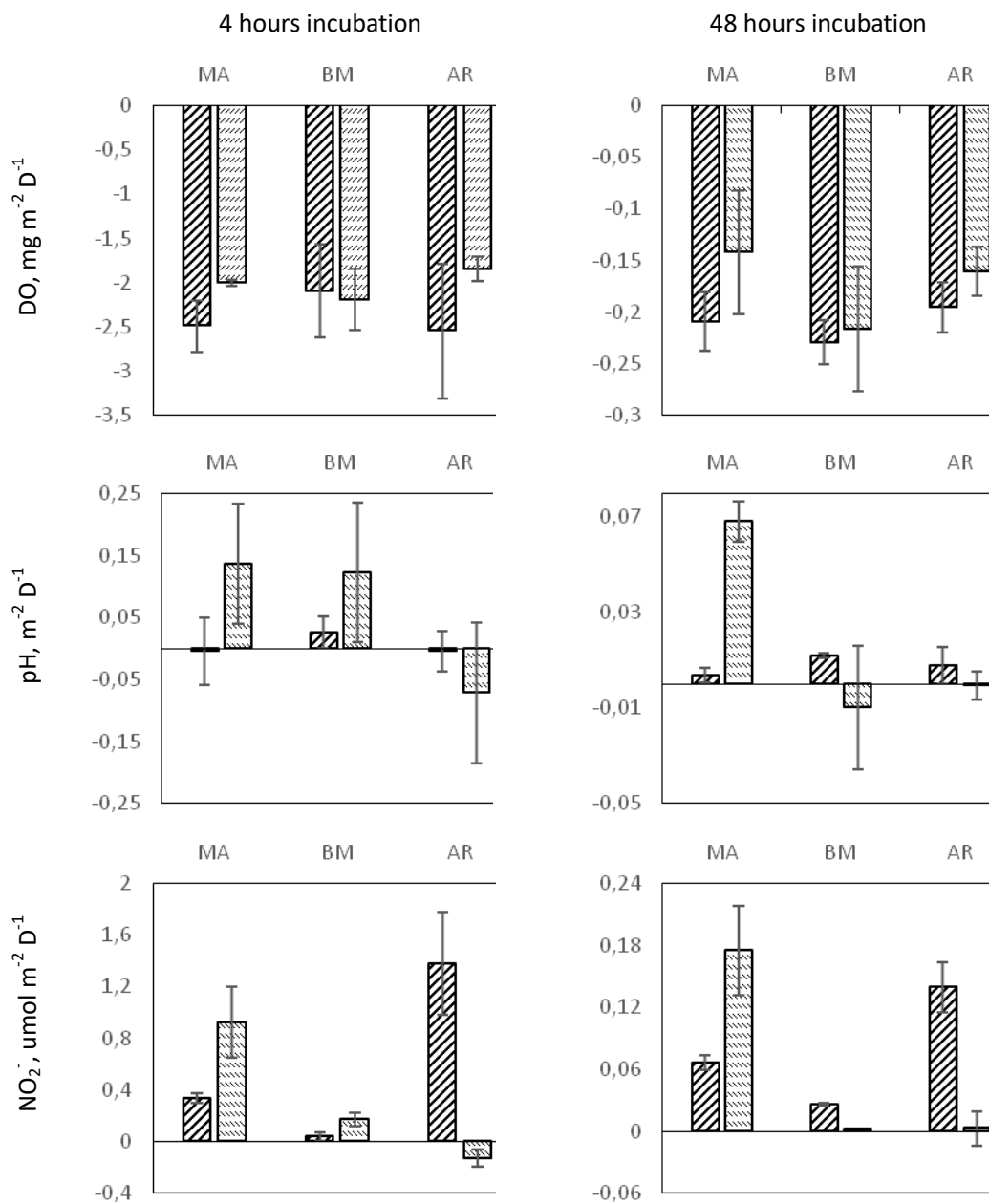


Figure 8. TN and TP in the pore water in the pore water after 8 and 48 h of incubation for spring and winter

Nutrient flux

DO and nutrient flux at sediment–water interface varied widely from release to uptake within 4 h and two days of incubation (Fig. 9). Oxygen and nutrient fluxes after the first 4 h of incubation were almost ten times higher than after the total 48 h of incubation. Oxygen flux varies over similar ranges in summer and winter, from -2.54 to -2.09 $\text{mg m}^{-2} \text{D}^{-1}$ and from -2.1888 to -1.8504 $\text{mg m}^{-2} \text{D}^{-1}$ after the first 4 h incubation. Significant differences ($p < 0.05$) were found between seasons at site MA in the first 4 h

of incubation, where higher oxygen fluxes were found in summer. The difference determined during the two seasons suggests that the higher oxygen consumption coincided with higher macroalgal decomposition, similar results were observed by Warnken et al. (2003). Nitrite fluxes were relatively low, in the range of 0.038 to 1.34 $\mu\text{mol m}^{-2} \text{D}^{-1}$ in summer and in the range of -0.1263 to 0.9210 $\mu\text{mol m}^{-2} \text{D}^{-1}$ in winter after the 4 h of incubation. Significant differences between seasons and among sites were observed. Nitrite uptake by the sediment after the first 4 h of incubation was demonstrated at site AR in winter. The maximum ammonium fluxes were recorded at site MA in winter after the first 4 h of incubation and at site BM in summer after the 48 h of incubation. Ammonium uptake by sediment was observed at site AR in both seasons after the 4 h of incubation. Phosphate exchange was generally very low, except for the high flux at site AR.



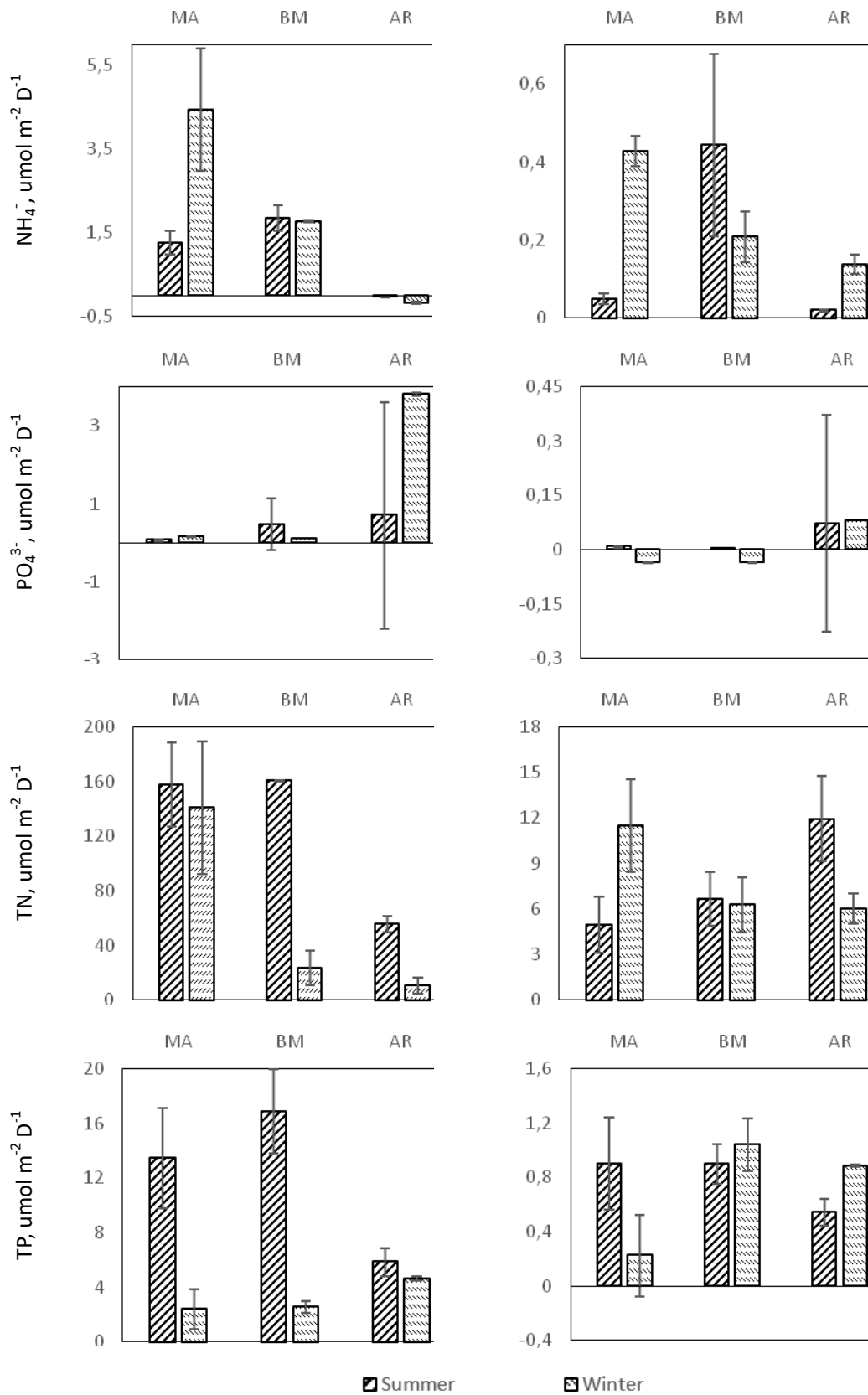


Figure 9. Oxygen, pH and nutrient flux after 4 h and 48 h of incubation in summer and winter

Average fluxes were in the range -0.1743 to $4.4478 \text{ } \mu\text{mol m}^{-2} \text{ D}^{-1}$. TN and TP were generally released from the sediment to the overlying water. A significant difference was observed between seasons after the 4 h of incubation, except at site MA. After 48 h of incubation, the highest TN and TP fluxes were recorded at site AR in summer, at site MA in winter, at site MA in summer and at site BM in winter.

Discussion

Benthos activities such as microorganism (Hines et al., 1982), shellfish (Castel, 1984; Chen et al., 2016b; 2005; Zhang et al., 2011; Zheng 2011), crabs (Zheng, 2011), and worms (Chen et al., 2016a) elicited rapid changes to nutrient exchange at sediment–water interface. These burrowing organisms bioturbate the sediment effectively flushing the nutrient and oxygen-rich water to considerable depth (Chen et al., 2016a; Miller, 1984; Rakotomalala et al., 2015). Spatial distribution of marine organisms in Zhelin Bay marine ranching area could be crucial to nutrient flux. Shu et al. (2015) reported that the *k*-dominance curve of macro-benthic abundance in Zhelin bay which showed that the seasonal trend in species diversity was winter > spring \approx autumn > summer. Otherwise, survey results showed that microbenthic in site BM was more than 2.0 times of site AR and 1.5 times of site MA (Chen et al., 2015), and highest molluscs density in site BM would be 200 ind. m^{-2} (Qin et al., 2016).

The pore water phosphate⁻ concentration showed a gradual increase with depth, and ammonium concentrations varied from 2.428 to $55.68 \text{ } \mu\text{mol L}^{-1}$ and from 1.996 to $54.03 \text{ } \mu\text{mol L}^{-1}$ in sites BM and MA respectively at both sites BM and MA for both seasons. Nitrite concentration showed a similar trend to ammonium. A similar trend was generally observed for nitrite concentration and phosphorus concentration (Denis and Grenz, 2003) and ammonia concentration (Sakamaki et al., 2006). Conversely, our results did not correspond with calculated in Bohai Bay coastal zone by Mu et al. (2016) who reported nitrite and DIN decreased with sediment depth.

Otherwise, decomposing organisms affected biogeochemical conditions of sediment (Chelsky et al., 2016; Wang et al., 2016). At site MA, higher nitrite, ammonia and phosphate fluxes were found in the winter, which was the same as the large scale macroalgae culture in this season. The high bloom of macroalgae would eventually become senescent and die. Decomposition of macroalgae stimulated sediment oxygen demand and an efflux of nitrogen and phosphorus (Wang et al., 2016). Welsh (2003) and Chelsky et al. (2016) study results showed that the physical barrier created by organism decomposition, reduces the transport of oxygen into the deeper sediment, however, our study did not show a similar trend. Benthic organisms, especially deposit feeders, will be present in this area and will be responsible for sediment reworking (Miller, 1984). This may explain the reason we found a similar trend in the MA and BM sites.

Moreover, hydrodynamics is an important factor that will influence sediment–surface water flux; a range of models has been used characteristics (Arndt et al., 2009; Bianchi et al., 2004; D'Itri, 1985; Gardner and Kjerfve, 2006; Hu and Li, 2009; Proctor et al., 2003). The phosphate flux at site AR in this experiment was higher than at the other sites. Also, if artificial reef deployment is to improve and increase fishery resources in the local area, then, it will affect the sediment–surface flux. In the early survey of Zhelin Bay ranching, the results showed higher fishery resources at site AR (Chen et al., 2015). Raoux et al. (2017) and Wu et al. (2016) also obtained higher

fishery resources in artificial reef area. These biological and physical changes are the main reasons which influence nutrient fluxes.

Conclusion

This preliminary study of different ecological functional zones used in marine ranching is useful for explaining the ecological function of different zones. Macroalgae decomposition showed the effect of overlying water nutrient concentration and nutrient fluxes which led to highest pH variation and highest nitrite, ammonia and total nitrogen fluxes in winter. As a presumed function of bioturbation in site BM, nutrient concentration in surface water increased quickly, while pore water nutrient kept in a stable level. Furthermore, artificial reef deployment changed the physical environment of sea bed and created upwelling at that area, which increased the flux of total phosphate. Our research results provide a basis for more specific studies towards the impacts on biological geochemistry of marine ranching construction. Further investigation should consider the physical feature of the sediment and induce biological species to study the bioturbation and physical changes of ecosystems.

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