Marine Pollution Bulletin 186 (2023) 114380

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Ocean acidification and warming significantly affect coastal eutrophication and organic pollution: A case study in the Bohai Sea

Yuqiu Wei [a,b], Dongsheng Ding [a,b], Ting Gu [c,d], Yong Xu [a,b], Xuemei Sun [a,b], Keming Qu [a,b], Jun Sun [c,d,*], Zhengguo Cui [a,b,**]

[a] Key Laboratory of Sustainable Development of Marine Fisheries, Ministry of Agriculture and Rural Affairs, Yellow Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences, Qingdao 266071, China

[b] Laboratory for Marine Fisheries Science and Food Production Processes, Pilot National Laboratory for Marine Science and Technology (Qingdao), Qingdao 266071, China

[c] Institute for Advanced Marine Research, China University of Geosciences, Guangzhou 511462, China

[d] Research Centre for Indian Ocean Ecosystem, Tianjin University of Science and Technology, Tianjin 300457, China

ARTICLE INFO

Keywords:
Climate change
Acidification
Warming
Eutrophication
Organic pollution

ABSTRACT

Most coastal ecosystems are faced with novel challenges associated with human activities and climate change such as ocean acidification, warming, eutrophication, and organic pollution. However, data on the independent or combined effects of ocean acidification and warming on coastal eutrophication and organic pollution at present are relatively limited. Here, we applied the generalized additive models (GAMs) to explore the dynamics of coastal eutrophication and organic pollution in response to future climate change in the Bohai Sea. The GAMs reflected the fact that acidification alone favors eutrophication and organic pollution, while warming alone inhibits these two variables. Differently, the interactions between acidification and warming in the future may further exacerbate the organic pollution but may mitigate the progress of eutrophication. These different responses of eutrophication and organic pollution to acidification and warming may be attributed to algae growth and microbial respiration, as well as some physical processes such as stratification.

1. Introduction

Rising atmospheric carbon dioxide (CO_2) primarily from anthropogenic sources (e.g., fossil fuel burning, tropical deforestation, and altered land use) has resulted in global warming, which is one of the most important environmental issues in today's ocean (Levitus et al., 2000; Kerr, 2007; Peters et al., 2013; Gao et al., 2019). Due to the natural equilibrium between gases in the atmosphere and ocean, these increased atmospheric CO_2 are absorbed by the ocean surface, decreasing ocean pH, and thus causing wholesale shifts in seawater carbonate chemistry, together referring to as ocean acidification (Guinotte and Fabry, 2008; Feely et al., 2009). Acidification is also a major environmental problem that has dramatic impacts on marine ecosystems and fisheries as well as human health (Sarmiento et al., 2004; Denman et al., 2011; Doney et al., 2020). In fact, acidification and warming are predictable consequences of rising atmospheric CO_2 and are unlikely to suffer from uncertainties associated with climate change forecasts (Doney et al., 2009). Accordingly, the processes of acidification and warming are well documented in time series data, hydrographic surveys, models and so forth, and their influences will further exacerbate over this century unless future CO_2 emissions are curbed dramatically (Levitus et al., 2000, 2005; Takahashi et al., 2006; Harrison and Carson, 2007; McNeil and Matear, 2008). There is growing evidence that acidification and warming have altered seawater physical and chemical properties and biogeochemical cycles of many elements and organisms. For example, warming of the surface ocean results in enhanced stratification, exposing plankton dwelling there to increased light radiation as well as to a decreased nutrient supply (Gao et al., 2019). In addition, various theoretical arguments based on laboratory and field studies have suggested that acidification leads to the lowering of calcium carbonate saturation states, thus decreasing the calcification rates of most calcifying algae and coral reefs (Hofmann et al., 2010; Sinutok et al., 2011). Taken together, the potential effects of acidification and warming on marine organisms and their broader implications for ocean ecosystems

* Correspondence to: J. Sun, Institute for Advanced Marine Research, China University of Geosciences, Guangzhou 511462, China.
** Correspondence to: Z. Cui, Yellow Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences, Qingdao 266071, China.
E-mail addresses: phytoplankton@163.com (J. Sun), cuizg@ysfri.ac.cn (Z. Cui).

https://doi.org/10.1016/j.marpolbul.2022.114380
Received 19 August 2022; Received in revised form 19 October 2022; Accepted 14 November 2022
Available online 29 November 2022

are not well known at present, and therefore both are high priorities for future researches.

Coastal marine ecosystems, which mainly include embayments, estuaries, salt marshes, mangroves, and shelves, are thought to be important to the sustainability of human development, because they could provide various beneficial services such as nutrient cycling, detoxification of pollutants, livelihood resources, economic trade, transportation, as well as human recreational activities (Costanza et al., 1997; Lu et al., 2018). However, growing human pressures, including rapid population growth and uncontrolled development, as well as dramatic advancement of human society and economy, are having profound, diverse, and irreversible consequences for trends of changes in these coastal marine environments (Freeman et al., 2019; Zhu et al., 2020). In recent decades, the rates of these changes have been rapid and potentially exceed the current capacities of many coastal ecosystems to adapt and/or recover, ultimately leading to severe environmental pollution and ecological devastation (Halpern et al., 2008, 2015). Of all these changes, eutrophication and organic pollution pose major threats to the coastal ecosystems worldwide, since the fluxes of nutrients and organic pollutants to coastal zones have risen substantially over the last decades (Howarth et al., 2011; Liu et al., 2011). At present, numerous laboratory, field, and model studies have revealed the global distribution, sources, drivers, and dynamics of eutrophication and organic pollution as well as their consequences on coastal marine ecosystems (Cloern, 2001; Troost et al., 2013; Lu et al., 2018; Deininger and Frigstad, 2019; Zhao et al., 2022). Also, there is accumulating evidence that eutrophication and organic pollution could increase the susceptibility of coastal waters to climate change. For instance, eutrophication may further exacerbate the acidified conditions of subsurface coastal waters (Cai et al., 2011; Wallace et al., 2014). Conceivably, the net effects of eutrophication and organic pollution may also depend on climate change as it also has far reaching consequences for coastal ecosystems (Sarmiento et al., 2004; Doney et al., 2012; Laurent et al., 2018). Therefore, a better understanding of coastal eutrophication and organic pollution is needed at several aspects, not only from the land-based human activities but also from climate change (e.g., ocean acidification and warming). However, previous studies on acidification, warming, eutrophication, and organic pollution in the Bohai Sea mainly focused on their dynamics and their impacts on the coastal ecosystem (Lin et al., 2001; Liu et al., 2011; Zhai et al., 2012; Zhang and Gao, 2016; Wang et al., 2018). For example, Liu et al. (2011) have reported that the organic pollutants from terrigenous inputs have a strong impact on the coastal waters of the Bohai Sea. To date, however, data on the independent or combined effects of climate change on coastal eutrophication and organic pollution are relatively limited in the Bohai Sea.

In the present study, hence we applied the generalized additive models to explore the existing relationships between coastal eutrophication and organic pollution and acidification and warming, and to project the dynamics of eutrophication and organic pollution in response to future climate change using a 3-year field measurement in the Bohai Sea, a semi-closed coastal sea that is affected by both human activities and climate change and that is important to biogeochemical cycles and fisheries. Here, we further proposed that ocean acidification and warming are likely to have a great impact on the dynamics of coastal eutrophication and organic pollution in the Bohai Sea. We also hope that our findings would provide a basis for understanding both the independent and combined effects of ocean acidification and warming on coastal eutrophication and organic pollution.

2. Materials and methods

2.1. Study area and sampling

There is accumulating evidence that water acidification, as a result of hypoxia, is in general a regional and seasonal phenomenon in the Bohai Sea, especially in the oxygen-depleted bottom waters (Zhai et al., 2012, 2019; Song et al., 2020; Gu et al., 2021). In this study, we similarly found that the pH had significantly declined during the past 3 years in the Bohai Sea, the indication being that acidification may be one of the major ecological problems in the study area (Supplementary Fig. S1). Although there is no significant inter-annual variability in average temperature during the study interval, the sea surface temperature in this region has annually increased by 0.011 °C in the past several decades (Lin et al., 2001; Wei et al., 2022b). These results suggest that ocean acidification and warming may have dramatic impacts on the Bohai Sea ecosystem and are likely to continue for many centuries (Harrison and Carson, 2007; Kerr, 2007; Guinotte and Fabry, 2008; Feely et al., 2009; Denman et al., 2011; Doney et al., 2020). Wang et al. (2018) have reviewed the historical changes in the situation of eutrophication and organic pollution in the China Seas from the end of the 1980s to the mid-2000s, and proposed that terrigenous inputs (including nutrients and organic matter) to coastal waters of the Bohai Sea has resulted in severe coastal eutrophication and organic pollution. Our earlier work also revealed that the seawater quality in the coastal Bohai Sea has reached the mild eutrophication level and is probably at risk from excessive nutrient loads (Wei et al., 2022a). Conceivably, the human-related pollutants entering the Bohai Sea are predicted to increase in the near future, and the degradation of water quality (e.g., eutrophication and organic pollution) in the Bohai Sea would thus become serious in the following years. Thus we feel confident in assuming that coastal eutrophication and organic pollution are two major problems in the Bohai Sea ecosystem in future ocean scenarios. Overall, available information makes the Bohai Sea an ideal region for understanding the potential effects of ocean acidification and warming on coastal eutrophication and organic pollution.

We thus conducted 12 oceanographic cruises spanning 3 years (2019–2021) in the Bohai Sea, China (38°N–40°N; 118°E–122°E) (Fig. 1). The cruises that employed same sampling strategies and analyses were undertaken in May, August, October, and December of each year between 2019 and 2021, representing spring, summer, autumn, and winter, respectively. A total of 41 sampling stations were located regularly in space and were all the same between cruises (Fig. 1). During each cruise, seawater samples were collected using 10-L Niskin bottles from three layers: the surface water (~2 m), the middle layer (~15–25), and the 2 m above bottom of the water column. Measurements of in situ temperature, pH, and dissolved oxygen (DO) were performed using a YSI multi-parameter water quality meter (ProDSS, USA). The calibrations of these three parameters were conducted following the standard methods detailed by Wei et al. (2022a). ~125 mL seawater samples for nutrient analysis were pre-filtered through 0.45 μm cellulose acetate membrane filters (47 mm), and then immediately frozen at −20 °C until processing. ~250 mL of seawater were collected for chemical oxygen demand (COD) analysis and also quickly frozen at −20 °C. Here all reported parameters were measured on water collected from the same Niskin bottles.

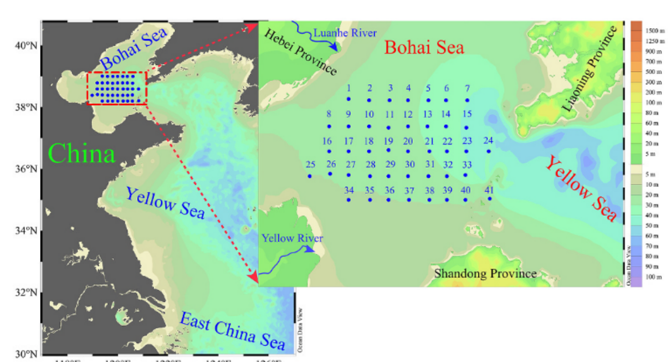

Fig. 1. Study area and sampling stations from 12 cruises in the Bohai Sea between May 2019 and December 2021.

2.2. Laboratory analysis

Analysis and determination of nutrient concentrations, including ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), and phosphate (PO_4^{3-}) were performed by a Technicon AA3 Auto-Analyzer (Bran + Luebbe, Norderstedt, Germany) according to the classical colorimetric methods (Crouch and Malmstadt, 1967; Verdouw et al., 1978; Dai et al., 2008). The detection limits of our AA3 Auto-Analyzer for NH_4^+, PO_4^{3-}, NO_3^-, and NO_2^- were 0.002, 0.002, 0.001, and 0.001 mg L^{-1}, respectively. In addition, DIN and DIP represented dissolved inorganic nitrogen (the sum of NH_4^+-N + NO_3^--N + NO_2^--N) and phosphate, respectively. The measurement of COD concentration was commonly performed according to the traditional standard method reported by Ma et al. (2016) and Li et al. (2018), i.e., the reflux digestion and $K_2Cr_2O_7$ titration.

2.3. Data analysis

2.3.1. Eutrophication status assessment

The eutrophication index (E_i) was applied to evaluate the eutrophication status of seawater. The E_i was calculated by the following evaluation formula (1), of which the eutrophication levels of seawater quality were defined as mild eutrophication ($1 \leq E_i \leq 3$), moderate eutrophication ($3 < E_i \leq 9$), and severe eutrophication ($E_i > 9$) (Zhu et al., 2020).

$$E_i = \frac{CCOD \times CDIN \times CDIP}{4500} \times 10^6 \quad (1)$$

where E_i is the eutrophication index, C_{COD}, C_{DIN}, and C_{DIP} are the measured concentrations (mg L^{-1}) of COD, DIN and DIP, respectively.

2.3.2. Comprehensive index of organic pollution

The degree of seawater organic pollution was identified applying the pollution index method (Liu et al., 2011), which comprehensively accounts for the effects of COD, DIN, DIP, and DO on seawater quality. The comprehensive index of organic pollution (C_i) was calculated by the following evaluation formula (2). For C_i, if $1 \leq C_i \leq 3$, the seawater is in slight degree of organic pollution situation; if $C_i > 3$, it is at severe pollution level.

$$C_i = \frac{C_{COD}}{C_{COD1}} + \frac{C_{DIN}}{C_{DIN1}} + \frac{C_{DIP}}{C_{DIP1}} - \frac{C_{DO}}{C_{DO1}} \quad (2)$$

where C_i is the organic pollution index, C_{COD}, C_{DIN}, C_{DIP}, and C_{DO} are the measured concentrations (mg L^{-1}) of COD, DIN, DIP, and DO, respectively; C_{COD1}, C_{DIN1}, C_{DIP1}, and C_{DO1} are the standard concentrations (i.e., 2, 0.2, 0.015, and 6 mg L^{-1}, respectively) as defined in Sea Water Quality Standard of China (Aqsiq, 1997).

2.4. Statistical analysis

To explore how acidification and warming influence the coastal eutrophication and organic pollution, we applied the generalized additive models (GAMs), which are constructed in R (v4.0.2) using the "mgcv" package with GCV smoothness estimation. Temperature and pH, which are most likely to change in the future and result in ocean acidification and warming (Doney et al., 2012; Xiao et al., 2018; Gao et al., 2019), were taken as potential explanatory variables, while E_i and C_i indices, which indicates the eutrophication level and the degree of organic pollution respectively (Liu et al., 2011; Zhu et al., 2020), were used as response variables. All statistical significance levels were set to $p < 0.05$.

3. Results

3.1. Variations in temperature, pH, E_i, and C_i

The seasonally varying climatic conditions, as well as regional riverine runoffs such as the Yellow River and Luanhe River (Fig. 1), have a great influence on the physicochemical properties of seawater in the Bohai Sea. Thus the dynamic trends of water temperature, pH, E_i, and C_i were relatively complex in our study area from May 2019 to December 2021 (Fig. 2). Water temperature in this region displayed a clear seasonal cycle in each year, with lowest in spring and winter and highest in summer (Fig. 2a). No significant warming phenomenon was observed in the study region over the past 3 years. This is not surprising because water temperature in the Bohai Sea increased by only 0.011 °C annually according to a 38-year temperature record (Lin et al., 2001). The water pH also showed a great fluctuation, especially the highest value during the spring and summer seasons (Fig. 2a). However, the pH values exhibited a descending trend from 2019 to 2021 (Supplementary Fig. S1), which indicated the acidified situation of the Bohai Sea.

The E_i index showed a large seasonal variation, reaching the maximum mostly during the autumn and winter seasons (Fig. 2b). Overall, the E_i values were within the limit of the standard for eutrophication status assessment from 2019 through 2021 (i.e., $E_i < 1$; Eq. (1)), the indication being that the entire surveyed area had not reached the eutrophication level during the past 3 years. Analogously, the C_i index also varied seasonally during 2019–2021, and the high values generally occurred in the autumn and winter seasons (Fig. 2b). The one exception was the summer of 2021, a period when C_i value was found to be the highest of the year. Most of the C_i values in the study area met the requirements of the water quality standard of organic pollution (i.e., $C_i < 1$; Eq. (2)). However, the C_i values exceeded the standard ($C_i > 1$) in October 2019 and December 2021, respectively, suggesting that this region was potentially confronting the problem of slight organic pollution in some cases. It is noteworthy that there was significant collinearity between E_i and C_i ($p < 0.01$; Supplementary Fig. S2), in large part because these two indices were both derived from COD, DIN, and DIP (Eqs. (1) & (2)). As such, the dynamics of E_i and C_i co-varied to some extent (Fig. 2b).

3.2. Partial effects of water temperature and pH on E_i and C_i

Water temperature was significantly correlated with both E_i and C_i with different relationships (Fig. 3a & b). The E_i index was negatively correlated with temperature at temperatures <10 °C, insensitive to temperature in the approximate range of 10–18 °C, and negatively

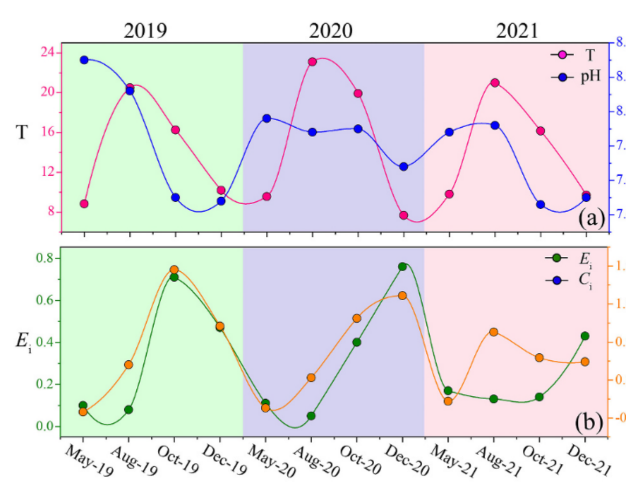

Fig. 2. Variations of temperature (°C), pH, E_i, and C_i in the Bohai Sea from May 2019 to December 2021. (a) T (i.e., temperature) and pH; (b) E_i and C_i.

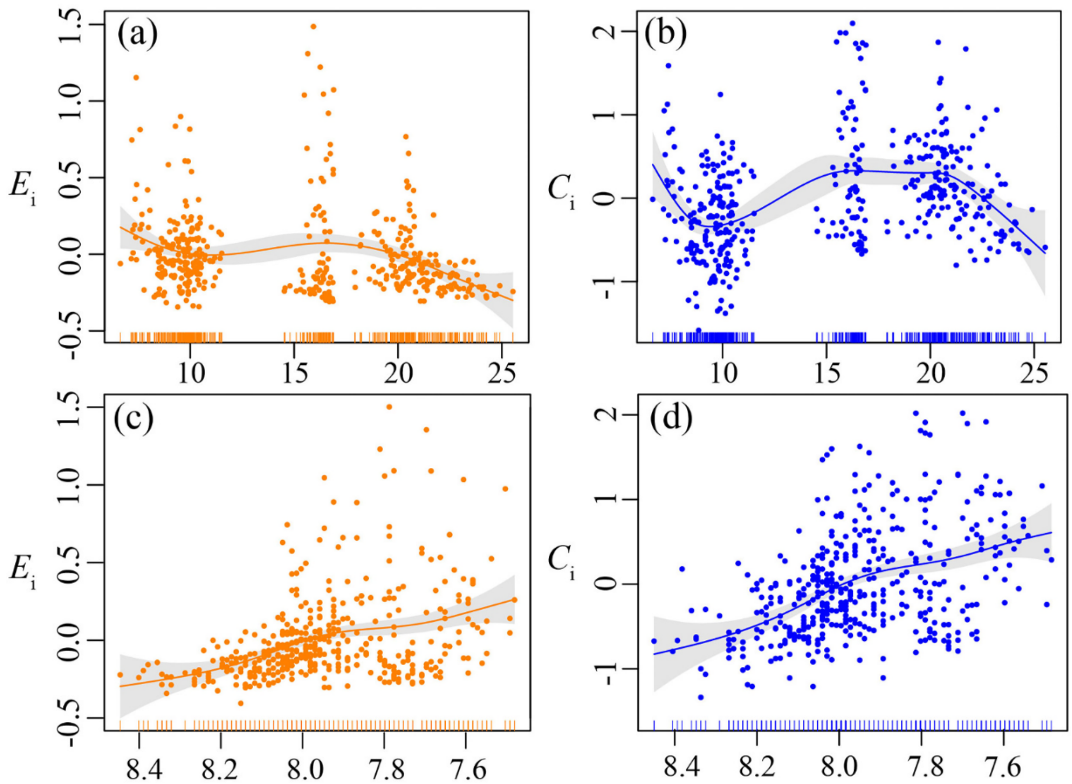

Fig. 3. Partial effects of water temperature and pH on E_i and C_i. (a, b) Partial effects of temperature (°C) on E_i and C_i. (c, d) Partial effects of water pH on E_i and C_i. The solid line is the smoother and the shaded areas are 95 % confidence bands.

correlated with temperature again at temperatures exceeding ~18 °C (Fig. 3a). The implication is that higher temperatures (i.e., ocean warming) would relieve the progress of coastal eutrophication. By comparison, the partial effect of temperature on C_i was significantly negative below ~10 °C but strongly positive between 10 and 15 °C (Fig. 3b), the clear indication being that C_i was more sensitive to temperature than E_i. There was a stable plateau of high C_i at temperatures of 15–20 °C, thereafter C_i was negatively correlated with temperature at temperatures exceeding ~20 °C. These results suggested that ocean warming would also mitigate the coastal organic pollution. Altogether, ocean warming appeared to have an inhibitory effect on the developments of coastal eutrophication and organic pollution.

Both E_i and C_i responded nonlinearly to water pH (Fig. 3c & d). Irrespective of the effect of other environmental factors, the partial effects of water pH on E_i and C_i were significant, and both E_i and C_i were positively correlated with pH decline. The implication is that lower pH (i.e., ocean acidification) was more likely to promote the coastal eutrophication and organic pollution. Along with the decline of water pH, the increase of C_i index at water pH < 8.0 was much more precipitous than the analogous increase of E_i index. This result revealed that E_i was less sensitive to water pH than C_i and that E_i was better able to tolerate ocean acidification than C_i. Overall, ocean acidification tended to exacerbate coastal eutrophication and organic pollution.

3.3. Combined effects of water temperature and pH on E_i and C_i

The responses of E_i and C_i to the interaction between water temperature and pH appeared more complex compared to the responses to

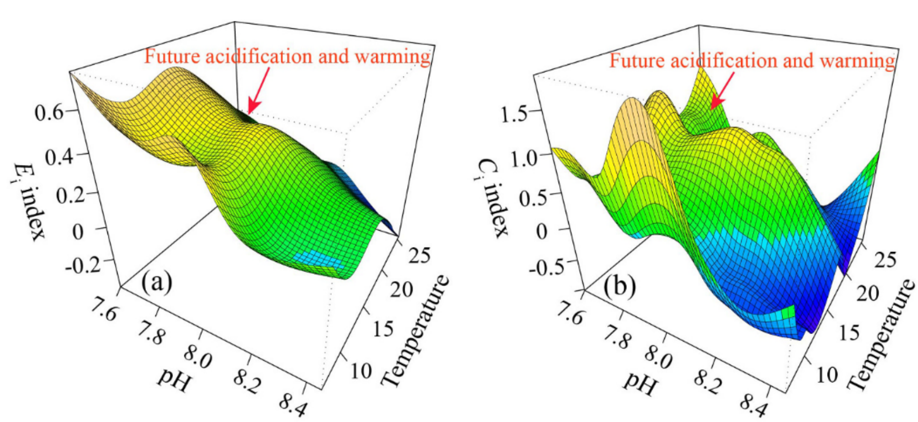

Fig. 4. Combined effects of water temperature (°C) and pH on (a) E_i and (b) C_i indices. The areas that the red arrows point to represent the future responses of eutrophication (E_i) and organic pollution (C_i) to the interactions between acidification (i.e., pH decline) and warming (i.e., increasing temperature). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

each single driver during the study interval (Fig. 4). Based on the raw data, our GAMs revealed that the interaction between temperature and pH was significantly correlated with both E_i and C_i ($p < 0.01$), indicating that coastal eutrophication and organic pollution were interactively affected by water temperature and pH. Therefore, future changes in the E_i and C_i as a result of the combined effects of ocean acidification and warming could be straightforward to anticipate. However, E_i and C_i varied greatly in response to the interact effect of the temperature increase and pH decline.

The E_i values decreased dramatically with rising temperature and declining pH, and finally remained relatively low at future conditions of temperature and pH (Fig. 4a). The implication is that future acidification combined with warming may have an antagonistic impact on the eutrophication status of the Bohai Sea. However, there was an obvious E_i peak at temperatures of ~15–20 °C, and the corresponding pH value was around 8.0, which is consistent with the partial effects of temperature and pH on E_i (Fig. 3a & c). Differently, the dynamic response of C_i to the interaction of water temperature and pH was rather complex (Fig. 4b). There were two obvious C_i peaks with increasing temperature and decreasing pH, of which one peak occurred in future climate scenarios. The implication is that the interaction between future changes of acidification and warming tend to have a synergistic effect on the coastal organic pollution. Additionally, this result further confirmed that C_i was more sensitive to temperature and pH than E_i (Fig. 3). Another peak of C_i occurred at temperatures of ~15–20 °C, and the corresponding pH value was around 8.0, which is quite similar to the peak of E_i. On the whole, these different future dynamics of E_i and C_i resulted from the fact that the interactive effects of acidification and warming would further exacerbate the coastal organic pollution rather than eutrophication.

4. Discussion

4.1. Effects of acidification and warming on coastal eutrophication and organic pollution

In the present study, despite existing difference in the responses of E_i and C_i to temperature and pH, there was significant collinearity between E_i and C_i ($p < 0.01$; Supplementary Fig. S2) due to the similarity of the derived parameters, e.g., COD, DIN, and DIP (Eqs. (1) & (2)). The implication is that coastal eutrophication and organic pollution and future changes in these two variables would co-vary, of which coastal eutrophication has been reported with increasing frequency in recent years. On the other hand, the organic matter in coastal waters is either produced internally or delivered from the terrestrial environment (Deininger and Frigstad, 2019). In other words, the sources of coastal organic pollution mainly include human-related organic pollutant inputs and excessive biological production of organic matter. However, the latter plays a crucial role for the coastal organic pollution and ecosystem health, since terrestrial organic matter is historically thought to be stable and relatively resistant to transformations within coastal ecosystems (Carlson and Hansell, 2015). Today, there is strong evidence that the development of excessive production of organic matter (e.g., phytoplankton blooms) is intrinsically induced by eutrophication as a result of human inputs of nutrients (Cai et al., 2011; Wallace et al., 2014). Given the close relationship between eutrophication and organic pollution as well as the key role of eutrophication on coastal ecosystems, we will only focus on the results of the effects of temperature and pH on eutrophication, while the responses of organic pollution to temperature and pH along with their interaction mechanism will not be discussed in detail below.

Globally rapid economic development and urbanization along the coastal zones have a profound impact on the stability and sustainability of the coastal ecosystems (Costanza et al., 1997; Sarmiento et al., 2004; Freeman et al., 2019). Eutrophication of coastal waters due to excessive nutrient loading is a consequence of anthropogenic activities, and also considered as one of the most threatening environmental problems worldwide (Cloern, 2001; Howarth et al., 2011; Wei et al., 2022a). Conceivably, such environmental problem is highly likely to further increase in the coming decades if no proper management strategies are implemented to balance or counteract the negative impacts of human activities (Halpern et al., 2008; Zhou et al., 2020; Zhu et al., 2020). Apart from the direct human-related pressures on coastal environments, it should be particularly noted that several natural variables (e.g., water temperature, local pH and atmospheric deposition) may also be partly or indirectly responsible for the coastal eutrophication (Paerl, 1997; Troost et al., 2013; Ngatia et al., 2017). Diverse evidence have pointed to atmospheric deposition as an important source of "new" nitrogen (N), which may play a key role in coastal eutrophication (Paerl, 1997; Troost et al., 2013). Moreover, some previous studies, despite inconsistent with our results, have provided tantalizing glimpses of the potential impacts that temperature and pH may have on eutrophication. For instance, the increase of global temperature could influence the balance between N removal and fixation in lakes, making them to be dominated by N fixation and thus increasing N-driven eutrophication level (Zhao et al., 2022). Low pH conditions in soil could alter the phosphorus (P) sorption through the formation of insoluble Al and Fe phosphates, reducing the amount of agricultural P sources into coastal waters, and to some extent mitigating P-induced eutrophication (Ngatia et al., 2017). These contrasting results are not surprising given that these differences in the responses of eutrophication to temperature or pH are attributable to the indirect effects. To date, however, relatively little is known about their direct effects on the coastal eutrophication.

Eutrophication in the semi-closed Bohai Sea has been deteriorating in the past 30 years owing to industrialization and urbanization along its coast as well as its limited water exchange with the outside (Song et al., 2020). Although our data indicated that the study region had not reached the eutrophication level, in many cases the E_i index (~0.8) was close to the limit of the standard for eutrophication status assessment (Fig. 2). Our earlier work also revealed that the Laizhou Bay, a region that is located in the Bohai Sea, is at risk from the eutrophication at present (Wei et al., 2022a). As well, we did not observe any warming phenomenon directly in the study area during the past 3 years, probably due to the lack of long-term observational data (Fig. 2). However, a previous study with respect to long-term variation of temperature from 1960 to 1997 has documented that the temperature increases by approximately 0.011 °C annually in the Bohai Sea (Lin et al., 2001). According to the data from the multi-scale ultrahigh resolution analysis, Guan et al. (2020) have also demonstrated that rapid warming has occurred in the Bohai Sea during 2002–2018. During the study interval, our study region was often relatively acidified (pH < 7.7; Wallace et al., 2014), especially the lower pH values frequently in the autumn and winter seasons (Fig. 2). The implication is that the acidification is a seasonal phenomenon in the Bohai Sea. In addition, the declining trend of pH levels between 2019 and 2021 (Supplementary Fig. S1) further confirmed that the Bohai Sea has experienced progressively acidification in recent years. This result is in line with previous studies that ocean acidification is a seasonal feature that often co-occurs with hypoxia in the Bohai Sea (Zhai et al., 2012; Song et al., 2020). Overall, the Bohai Sea is an ideal study region for understanding the direct effects of temperature and pH on the coastal eutrophication. In the present study, our findings revealed that temperature and pH significantly affect the eutrophication level in the Bohai Sea. As such, this study provides new insight regarding the independent and combined effects of ocean acidification and warming on coastal eutrophication as well as evidence that other natural variables than human activities are also be partly responsible for coastal eutrophication.

Based on the raw data, our GAMs revealed that ocean warming seems likely to mitigate the progress of coastal eutrophication (Fig. 3). Although the mechanism of warming affecting eutrophication is not clear at present, ocean warming that would entail phytoplankton to consume substantial amounts of nutrients (especially N and P) may provide a possible rationale for the observed relationship between warming and eutrophication. Here, we therefore proposed a bold assumption that whether warming increases the N and P utilization of phytoplankton, thereby indirectly mitigating the coastal eutrophication. It has been well known that coastal zones have received large amounts of N and P nutrients that results in eutrophication (Cloern, 2001; Howarth et al., 2011; Laurent et al., 2018). Both N and P are essential nutrients for the growth and metabolism of phytoplankton, while in most cases phytoplankton are limited by N and/or P (Wei et al., 2017). As a result, eutrophication associated with the inputs of N and P would significantly stimulate phytoplankton primary production (Gao et al., 1998). Numerous studies have shown that warming and eutrophication could combine to further improve the growth and metabolic rates of phytoplankton and ultimately induce the increases in the magnitude and occurrence of phytoplankton blooms (e.g., harmful algal blooms) (Winder and Sommer, 2012; Xiao et al., 2018; Lee et al., 2019). It is notable that this process would reduce nutrient availability and indirectly mitigate eutrophication in coastal ecosystems. Furthermore, warming may result in enhanced stratification of upper mixed layers and thus decreased upward transport of nutrients from deeper layers (Gao et al., 2019), which in turn can lead to nutrient limitation and may also alleviate eutrophication to some extent. Despite lacking direct evidence, those previous studies above regarding the decrease in nutrients associated with ocean warming can provide an invaluable glimpse into the relationship between warming and eutrophication.

The opposite correspondence between pH and E_i (Fig. 3) and the occurrence of low pH conditions (Fig. 2) in the study region indicated that acidification tended to exacerbate coastal eutrophication. Likewise, the mechanism of acidification affecting eutrophication is also unknown at present. However, some previous studies regarding coastal eutrophication associated with the development of acidification may provide some insights. During microbial respiration, excessive consumption of organic matter induced by eutrophication (as discussed above) in coastal waters lowers oxygen levels, meanwhile the consequence of this process is the production of CO_2 and a lowering of seawater pH (Cai et al., 2011; Zhai et al., 2012; Wallace et al., 2014). In turn, raising seawater CO_2 concentrations (i.e., acidification) as a result of increasing atmospheric CO_2 would inhibit microbial respiration, reducing the consumption of algae-driven organic matter. Conceivably, the excessive organic matter contained all the carbon and nutrients therein would be recycled within the coastal waters, which has the potential to release large amounts of N and P and further worsen eutrophication. In addition, our earlier work has demonstrated that high levels of pCO_2 in seawater can facilitate the NPQ (i.e., Non-photochemical quenching) process of phytoplankton, ultimately leading to reduced primary production (Wei et al., 2021). This process may reduce the consumption of N and P, potentially exacerbating coastal eutrophication. Altogether, these assumptions lead us to conclude that acidification may worsen eutrophication by altering phytoplankton growth and microbial respiration. However, more data are needed to further explore the mechanistic roles of ocean acidification and warming on coastal eutrophication and organic pollution, as well as providing a novel context of climate changes to those interested in changing marine environment.

4.2. *Future changes of coastal eutrophication and organic pollution*

Irrespective of other environmental variables, our GAMs revealed that ocean acidification and warming in the future would interactively promote coastal organic pollution, but inhibit the progress of coastal eutrophication (Fig. 4). However, we also found that acidification alone favored coastal eutrophication and organic pollution, while warming alone inhibited them (Fig. 3). These results lead us to speculate that such interactions, including the synergistic and antagonistic patterns, fundamentally alter the mechanisms of coastal eutrophication and organic pollution in response to temperature and pH, compared to their responses to each single driver. Certainly, some previous studies with respect to the combined impacts of acidification, warming, eutrophication, stratification, deoxygenation and so forth on photosynthetic organisms have provided some insights into our above assumption. For example, ocean warming combined with eutrophication would have complex consequences for phytoplankton communities due to altered balance between the processes that are driven by nutrient supply and metabolic rates (Xiao et al., 2018). For some marine algae, the interactive effects of acidification and warming could be manifested as pH decline changing their inherent metabolic tolerance to temperature changes (Gao et al., 2019). Overall, future acidification and warming are likely to interactively alter the inherent tolerance of coastal systems to eutrophication and organic pollution or their capacity to cope with these environmental problems, as long as without the additional stress.

The GAMs reflected the fact that the coastal eutrophication became weaker but the organic pollution became stronger, with increasing temperature and decreasing pH. Projecting the future changes of coastal eutrophication and organic pollution requires knowing what will happen to these two environmental problems as a result of ocean acidification combined with warming. Although the E_i and C_i had some collinearity or some degree of correlation, their future patterns in fact seem reasonable if we assume that the difference between changes in E_i and C_i is attributable to the explanatory variable of DO, a derived-parameter that is used to estimate C_i instead of E_i (Eqs. (1) & (2)). In accord with this logic, understanding of the relationships between DO and temperature and pH is important to predict the future response of organic pollution to combined effects of acidification and warming. Analysis of our data from the Bohai Sea revealed that DO is positively correlated with pH and negatively correlated with temperature (Fig. 5). The implication is that both ocean acidification and warming can significantly contribute to the hypoxia, much less their combined effects. Analysis of the data collected from the Gulf of Mexico and the East China Sea (Cai et al., 2011) also revealed a significant positive correlation between pH and DO, further linking the intensified acidification to oxygen consumption via organic-matter oxidation. In addition, recent studies suggest that the O_2 levels in the eastern Pacific have declined over the past 50 years due to ocean warming (Whitney et al., 2007). Ocean models also predict declines of 1 to 7 % in the global ocean O_2 inventory over the next century under the influence of future warming and stratification of the upper ocean (Keeling et al., 2010). Conceivably, the hypoxic conditions as a result of the interactive effects of acidification and warming would in turn inhibit the action of microbes as well as their consumption of excessive organic matter, leading to the decoupling between primary production and respiration in the surface water. Subsequent accumulation and aggregation of organic matter may further exacerbate the coastal organic pollution. However, it is not clear why coastal eutrophication negatively responds to the double stresses of projected acidification and warming. Certainly, future changes in coastal eutrophication may also have even more serious implications than the change we have projected. These problems are worth serious investigation in the future.

CRediT authorship contribution statement

Yuqiu Wei: Data curation, Writing – original draft, Writing – review & editing. **Dongsheng Ding:** Investigation, Formal analysis, Writing – review & editing. **Ting Gu:** Data curation, Formal analysis. **Yong Xu:** Investigation. **Xuemei Sun:** Investigation. **Keming Qu:** Formal analysis, Writing – review & editing. **Jun Sun:** Formal analysis, Writing – review & editing. **Zhengguo Cui:** Conceptualization, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

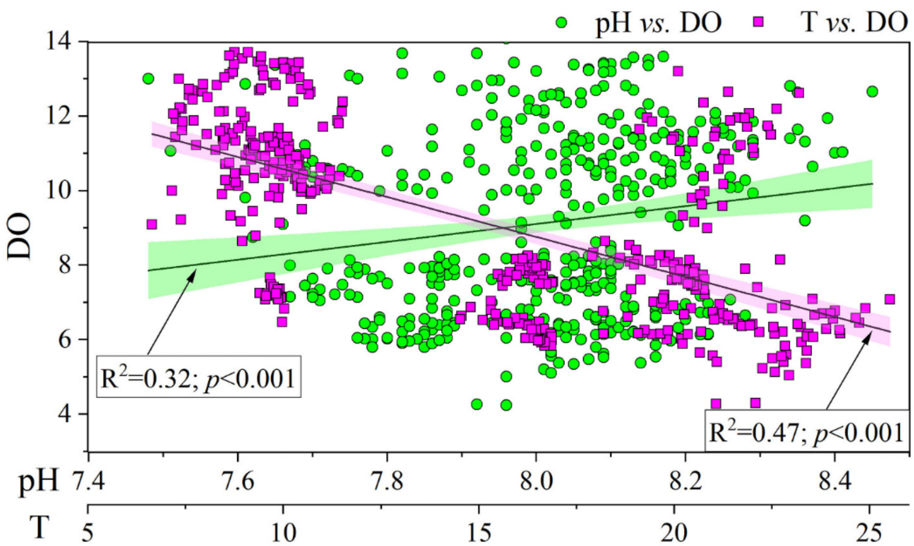

Fig. 5. Significant relationships between DO (mg L^{-1}) and temperature (T; °C) and pH. The black lines represent the least square regression, which is statistically significant for both cases (R^2 and *p*-value). Shaded areas are 95 % confidence bands.

Data availability

Data will be made available on request.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (42206103), the Project funded by China Post-doctoral Science Foundation (2021M703590), the Shandong Post-doctoral Innovation Talent Support Program (SDBX2021014), the Shandong Natural Science Foundation (ZR2022QD133), the Central Public-interest Scientific Institution Basal Research Fund, YSFRI, CAFS (2020TD49 & 20603022022010), and the Qingdao Postdoctoral Applied Research Project to YW. Also, we would like to show our great gratitude to all members of Yellow Sea & Bohai Sea Fishery Ecological Environment Monitoring Center for their assistance in our sampling and analysis processes.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2022.114380.

References

Aqsiq, P., 1997. Sea Water Quality Standard, GB 3097-1997. General Administration of Quality Supervision, Inspection and Quarantine of People's Republic of China.

Cai, W.J., Hu, X., Huang, W.J., Murrell, M.C., Lehrter, J.C., Lohrenz, S.E., Gong, G.C., 2011. Acidification of subsurface coastal waters enhanced by eutrophication. Nat. Geosci. 4 (11), 766–770.

Carlson, C.A., Hansell, D.A., 2015. DOM sources, sinks, reactivity, and budgets. In: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Elsevier, Amsterdam, pp. 65–126.

Cloern, J.E., 2001. Our evolving conceptual model of the coastal eutrophication problem. Mar. Ecol. Prog. Ser. 210, 223–253.

Costanza, R., d'Arge, R., De Groot, R., Farber, S., Grasso, M., Hannon, B., Van Den Belt, M., 1997. The value of the world's ecosystem services and natural capital. Nature 387 (6630), 253–260.

Crouch, S.R., Malmstadt, H.V., 1967. Mechanistic investigation of molybdenum blue method for determination of phosphate. Anal. Chem. 39 (10), 1084–1089.

Dai, M., Wang, L., Guo, X., Zhai, W., Li, Q., He, B., Kao, S.J., 2008. Nitrification and inorganic nitrogen distribution in a large perturbed river/estuarine system: the Pearl River Estuary, China. Biogeosciences 5 (5), 1227–1244.

Deininger, A., Frigstad, H., 2019. Reevaluating the role of organic matter sources for coastal eutrophication, oligotrophication, and ecosystem health. Front. Mar. Sci. 6, 210.

Denman, K., Christian, J.R., Steiner, N., Pörtner, H.O., Nojiri, Y., 2011. Potential impacts of future ocean acidification on marine ecosystems and fisheries: current knowledge and recommendations for future research. ICES J. Mar. Sci. 68 (6), 1019–1029.

Doney, S.C., Fabry, V.J., Feely, R.A., Kleypas, J.A., 2009. Ocean acidification: the other CO2 problem. Annu. Rev. Mar. Sci. 1, 169–192.

Doney, S.C., Ruckelshaus, M., Duffy, J.E., Barry, J.P., Chan, F., English, C.A., Talley, L.D., 2012. Climate change impacts on marine ecosystems. Annu. Rev. Mar. Sci. 4, 11–37.

Doney, S.C., Busch, D.S., Cooley, S.R., Kroeker, K.J., 2020. The impacts of ocean acidification on marine ecosystems and reliant human communities. Annu. Rev. Environ. Resour. 5 (1).

Feely, R.A., Doney, S.C., Cooley, S.R., 2009. Ocean acidification: present conditions and future changes in a high-CO_2 world. Oceanography 22 (4), 36–47.

Freeman, L.A., Corbett, D.R., Fitzgerald, A.M., Lemley, D.A., Quigg, A., Steppe, C.N., 2019. Impacts of urbanization and development on estuarine ecosystems and water quality. Estuar. Coasts 42 (7), 1821–1838.

Gao, H., Feng, S., Guan, Y., 1998. Modelling annual cycles of primary production in different regions of the Bohai Sea. Fish. Oceanogr. 7 (3–4), 258–264.

Gao, K., Beardall, J., Häder, D.P., Hall-Spencer, J.M., Gao, G., Hutchins, D.A., 2019. Effects of ocean acidification on marine photosynthetic organisms under the concurrent influences of warming, UV radiation, and deoxygenation. Front. Mar. Sci. 6, 322.

Gu, T., Jia, D., Ma, X., Peng, L., Zhang, G., Wei, Y., Sun, J., 2021. Hypoxia-enhanced N2O production under ocean acidification in the Bohai Sea. Front. Mar. Sci. 8, 695105.

Guan, L., Shan, X., Jin, X., Gorfine, H., Yang, T., Li, Z., 2020. Evaluating spatio-temporal dynamics of multiple fisheries-targeted populations simultaneously: a case study of the Bohai Sea ecosystem in China. Ecol. Model. 422, 108987.

Guinotte, J.M., Fabry, V.J., 2008. Ocean acidification and its potential effects on marine ecosystems. Ann. N. Y. Acad. Sci. 1134 (1), 320–342.

Halpern, B.S., Walbridge, S., Selkoe, K.A., Kappel, C.V., Micheli, F., d'Agrosa, C., Watson, R., 2008. A global map of human impact on marine ecosystems. Science 319 (5865), 948–952.

Halpern, B.S., Frazier, M., Potapenko, J., Casey, K.S., Koenig, K., Longo, C., Walbridge, S., 2015. Spatial and temporal changes in cumulative human impacts on the world's ocean. Nat. Commun. 6 (1), 1–7.

Harrison, D.E., Carson, M., 2007. Is the world ocean warming? Upper-ocean temperature trends: 1950–2000. J. Phys. Oceanogr. 37 (2), 174–187.

Hofmann, G.E., Barry, J.P., Edmunds, P.J., Gates, R.D., Hutchins, D.A., Klinger, T., Sewell, M.A., 2010. The effect of ocean acidification on calcifying organisms in marine ecosystems: an organism-to-ecosystem perspective. Annu. Rev. Ecol. Evol. Syst. 127–147.

Howarth, R., Chan, F., Conley, D.J., Garnier, J., Doney, S.C., Marino, R., Billen, G., 2011. Coupled biogeochemical cycles: eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. Front. Ecol. Environ. 9 (1), 18–26.

Keeling, R.F., Körtzinger, A., Gruber, N., 2010. Ocean deoxygenation in a warming world. Annu. Rev. Mar. Sci. 2 (1), 199–229.

Kerr, R.A., 2007. Global warming is changing the world. Science 316 (5822), 188–190.

Laurent, A., Fennel, K., Ko, D.S., Lehrter, J., 2018. Climate change projected to exacerbate impacts of coastal eutrophication in the northern Gulf of Mexico. J. Geophys. Res. Oceans 123 (5), 3408–3426.

Lee, K.H., Jeong, H.J., Lee, K., Franks, P.J., Seong, K.A., Lee, S.Y., Kim, K.Y., 2019. Effects of warming and eutrophication on coastal phytoplankton production. Harmful Algae 81, 106–118.

Levitus, S., Antonov, J.I., Boyer, T.P., Stephens, C., 2000. Warming of the world ocean. Science 287 (5461), 2225–2229.

Levitus, S., Antonov, J., Boyer, T., 2005. Warming of the world ocean, 1955–2003. Geophys. Res. Lett. 32 (2).
Li, J., Luo, G., He, L., Xu, J., Lyu, J., 2018. Analytical approaches for determining chemical oxygen demand in water bodies: a review. Crit. Rev. Anal. Chem. 48 (1), 47–65.
Lin, C., Su, J., Xu, B., Tang, Q., 2001. Long-term variations of temperature and salinity of the Bohai Sea and their influence on its ecosystem. Prog. Oceanogr. 49 (1–4), 7–19.
Liu, S., Lou, S., Kuang, C., Huang, W., Chen, W., Zhang, J., Zhong, G., 2011. Water quality assessment by pollution-index method in the coastal waters of Hebei Province in western Bohai Sea, China. Mar. Pollut. Bull. 62 (10), 2220–2229.
Lu, Y., Yuan, J., Lu, X., Su, C., Zhang, Y., Wang, C., Sweijd, N., 2018. Major threats of pollution and climate change to global coastal ecosystems and enhanced management for sustainability. Environ. Pollut. 239, 670–680.
Ma, Y., Tie, Z., Zhou, M., Wang, N., Cao, X., Xie, Y., 2016. Accurate determination of low-level chemical oxygen demand using a multistep chemical oxidation digestion process for treating drinking water samples. Anal. Methods 8 (18), 3839–3846.
McNeil, B.I., Matear, R.J., 2008. Southern Ocean acidification: a tipping point at 450-ppm atmospheric CO2. Proc. Natl. Acad. Sci. 105 (48), 18860–18864.
Ngatia, L.W., Hsieh, Y.P., Nemours, D., Fu, R., Taylor, R.W., 2017. Potential phosphorus eutrophication mitigation strategy: biochar carbon composition, thermal stability and pH influence phosphorus sorption. Chemosphere 180, 201–211.
Paerl, H.W., 1997. Coastal eutrophication and harmful algal blooms: importance of atmospheric deposition and groundwater as "new" nitrogen and other nutrient sources. Limnol. Oceanogr. 42 (5part2), 1154–1165.
Peters, G.P., Andrew, R.M., Boden, T., Canadell, J.G., Ciais, P., Le Quéré, C., Wilson, C., 2013. The challenge to keep global warming below 2 C. Nat. Clim. Chang. 3 (1), 4–6.
Sarmiento, J.L., Slater, R., Barber, R., Bopp, L., Doney, S.C., Hirst, A.C., Stouffer, R., 2004. Response of ocean ecosystems to climate warming. Glob. Biogeochem. Cycl. 18 (3).
Sinutok, S., Hill, R., Doblin, M.A., Wuhrer, R., Ralph, P.J., 2011. Warmer more acidic conditions cause decreased productivity and calcification in subtropical coral reef sediment-dwelling calcifiers. Limnol. Oceanogr. 56 (4), 1200–1212.
Song, G., Zhao, L., Chai, F., Liu, F., Li, M., Xie, H., 2020. Summertime oxygen depletion and acidification in Bohai Sea, China. Frontiers in Marine Science 7, 252.
Takahashi, T., Sutherland, S.C., Feely, R.A., Wanninkhof, R., 2006. Decadal change of the surface water pCO2 in the North Pacific: a synthesis of 35 years of observations. J. Geophys. Res. Oceans 111 (C7).
Troost, T.A., Blaas, M., Los, F.J., 2013. The role of atmospheric deposition in the eutrophication of the North Sea: a model analysis. J. Mar. Syst. 125, 101–112.
Verdouw, H., Van Echteld, C.J.A., Dekkers, E.M.J., 1978. Ammonia determination based on indophenol formation with sodium salicylate. Water Res. 12 (6), 399–402.
Wallace, R.B., Baumann, H., Grear, J.S., Aller, R.C., Gobler, C.J., 2014. Coastal Ocean acidification: the other eutrophication problem. Estuar. Coast. Shelf Sci. 148, 1–13.
Wang, B., Xin, M., Wei, Q., Xie, L., 2018. A historical overview of coastal eutrophication in the China seas. Mar. Pollut. Bull. 136, 394–400.
Wei, Y., Liu, H., Zhang, X., Xue, B., Munir, S., Sun, J., 2017. Physicochemical conditions in affecting the distribution of spring phytoplankton community. Chin. J. Oceanol. Limnol. 35 (6), 1342–1361.
Wei, Y., Zhao, Y., Gui, J., Sun, J., 2021. Phosphorus enrichment masked the negative effects of ocean acidification on picophytoplankton and photosynthetic performance in the oligotrophic Indian Ocean. Ecol. Indic. 125, 107459.
Wei, Y., Cui, H., Hu, Q., Bai, Y., Qu, K., Sun, J., Cui, Z., 2022a. Eutrophication status assessment in the Laizhou Bay, Bohai Sea: further evidence for the ecosystem degradation. Mar. Pollut. Bull. 181, 113867.
Wei, Y., Ding, D., Gu, T., Jiang, T., Qu, K., Sun, J., Cui, Z., 2022b. Different responses of phytoplankton and zooplankton communities to current changing coastal environments. Environ. Res. 215, 114426.
Whitney, F.A., Freeland, H.J., Robert, M., 2007. Persistently declining oxygen levels in the interior waters of the eastern subarctic Pacific. Prog. Oceanogr. 75 (2), 179–199.
Winder, M., Sommer, U., 2012. Phytoplankton response to a changing climate. Hydrobiologia 698 (1), 5–16.
Xiao, W., Liu, X., Irwin, A.J., Laws, E.A., Wang, L., Chen, B., Huang, B., 2018. Warming and eutrophication combine to restructure diatoms and dinoflagellates. Water Res. 128, 206–216.
Zhai, W., Zhao, H., Zheng, N., Xu, Y., 2012. Coastal acidification in summer bottom oxygen-depleted waters in northwestern-northern Bohai Sea from June to August in 2011. Chin. Sci. Bull. 57 (9), 1062–1068.
Zhai, W.D., Zhao, H.D., Su, J.L., Liu, P.F., Li, Y.W., Zheng, N., 2019. Emergence of summertime hypoxia and concurrent carbonate mineral suppression in the central Bohai Sea, China. Journal of Geophysical Research: Biogeosciences 124 (9), 2768–2785.
Zhang, J., Gao, X., 2016. Nutrient distribution and structure affect the acidification of eutrophic ocean margins: A case study in southwestern coast of the Laizhou Bay, China. Marine Pollution Bulletin 111 (1-2), 295–304.
Zhao, F., Zhan, X., Xu, H., Zhu, G., Zou, W., Zhu, M., Tang, W., 2022. New insights into eutrophication management: importance of temperature and water residence time. J. Environ. Sci. 111, 229–239.
Zhou, Y., Wang, L., Zhou, Y., Mao, X.Z., 2020. Eutrophication control strategies for highly anthropogenic influenced coastal waters. Sci. Total Environ. 705, 135760.
Zhu, G., Noman, M.A., Narale, D.D., Feng, W., Pujari, L., Sun, J., 2020. Evaluation of ecosystem health and potential human health hazards in the Hangzhou Bay and Qiantang Estuary region through multiple assessment approaches. Environ. Pollut. 264, 114791.