


 Cite this: *RSC Adv.*, 2026, 16, 714

Interannual variability of oceanic pH in a highly human-perturbed bay in China

 Ping Han,^{abc} Jin Wang ^{*cde} and Feiyong Chen^{de}

Due to anthropogenic carbon dioxide (CO₂) emissions, open oceans are acidifying, and the acidification rate is relatively stable. While coastal waters experience even greater pH fluctuations from terrestrial inputs, upwelling, and biological activity, this variability necessitates detailed long-term research in these regions. Based on field observations and historical literature data from 1980 to 2016, the interannual variability of seawater pH and its driving mechanisms were analyzed in Jiaozhou Bay, a highly human-perturbed bay in China. The results revealed an overall decreasing trend in pH over the three-decade period, with a decline rate of 0.0062 years⁻¹, which is 3.6 times faster than that observed in the open ocean, indicating significant anthropogenic impacts on pH variations in Jiaozhou Bay. The long-term pH changes showed strong correlations with coastal environmental pollution status, characterized by three distinct phases: a decline from 1980 to 1986, followed by an increase during 1991 to 2004, and subsequently another decreasing trend from 2004 to 2016. Terrestrial (including wastewater) inputs were identified as predominant anthropogenic factors influencing these pH variations. Furthermore, this study highlights that while future management should focus on reducing organic matter and nutrient inputs, particular attention should be paid to the direct impacts of dissolved inorganic carbon (DIC) from treated wastewater discharge on pH reduction.

 Received 1st November 2025
 Accepted 15th December 2025

DOI: 10.1039/d5ra08399k

rsc.li/rsc-advances

1. Introduction

The absorption of anthropogenic atmospheric CO₂ by the ocean has partially mitigated global warming,¹ yet it has simultaneously triggered another critical environmental issue: ocean acidification. It is reported that seawater pH remained above 8.1 for over 20 million years.² However, since the Industrial Revolution, the oceanic uptake of atmospheric CO₂ has reduced seawater pH by approximately 0.1 units within just two centuries, equivalent to a 30% increase in seawater acidity.³ Furthermore, IPCC model projections indicate that surface seawater pH will decrease by an additional 0.3–0.4 units by the end of this century, resulting in seawater acidity reaching 100%~150% of pre-industrial levels. Ocean acidification profoundly impacts multiple biochemical properties of

seawater, including chemical reactions, equilibrium processes, and alterations in biological toxicity.¹

Numerous observational datasets from open ocean have elucidated long-term trends in seawater pH. For instance, pH in the Atlantic and Pacific Oceans has exhibited a declining trend during 1995–2004 and 1983–2005, with long-term reduction rates of ~0.0017 units years⁻¹ ref. 3 and 4 At the ALOHA station in the central North Pacific mixed layer, pH decreased by an average of 0.0019 units years⁻¹ between 1991 and 2006,⁵ consistent with model-predicted surface pH decline rates of 0.0013–0.002 units years⁻¹.⁶

In contrast, coastal regions demonstrate divergent rates and trends in long-term pH variability. Wootton *et al.* reported a pH decline rate of 0.045 units years⁻¹ through an 8 year pH monitoring program along the U.S. West Coast, significantly exceeding open ocean acidification rates.⁷ Brutemark *et al.* analyzed pH time-series data (1972–2009) from the western Gulf of Finland, revealing a winter pH decline of ~0.006 units years⁻¹.⁸ Provoost *et al.* documented pH reduction rates in Dutch coastal waters that substantially surpassed open ocean trends, with distinct regional variability: pH in the North Sea, Wadden Sea, Eastern Scheldt, and Western Scheldt exhibited initial increases followed by decreases, while the Ems-Dollard estuary maintained a persistent upward trend.⁹ These findings highlight that coastal pH dynamics are characterized by greater variability and complexity compared to open ocean systems, underscoring the necessity for dedicated investigations into

^aDepartment of Ecological Protection and Environmental Engineering, Shandong Urban Construction Vocational College, Jinan 250103, China. E-mail: hanping900304@163.com

^bJinan Ecological & Environmental Monitoring Center of Shandong Province, Jinan 250100, China. E-mail: hanping900304@163.com

^cKey Laboratory of Marine Environment and Ecology, Ministry of Education, College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China. E-mail: hanping900304@163.com; wangjin21@sdjzu.edu.cn

^dResearch Institute of Resources and Environment Innovation, Shandong Jianzhu University, Jinan, China. E-mail: wangjin21@sdjzu.edu.cn

^eHainan Flexible Talent Introduction and Innovation Platform, Hainan 570228, China



long-term pH trends and controlling mechanisms in nearshore environments.

Jiaozhou Bay, a temperate semi-enclosed shallow bay under intense urbanization pressure, experiences combined natural and anthropogenic perturbations. The eastern bay is influenced by wastewater discharges, while the western bay is affected by riverine inputs and mariculture activities. Based on long-term observational datasets and literature data, this study examined the multi-decadal pH variability in Jiaozhou Bay from 1980 to 2016, and provided preliminary analyses of underlying drivers.

2. Materials and methods

2.1 Study area

Jiaozhou Bay ($35^{\circ}57' - 36^{\circ}18' \text{N}$, $120^{\circ}04' - 120^{\circ}23' \text{E}$), located on the southern coast of the Shandong Peninsula, is semi-enclosed by land on its eastern, western, and northern boundaries, with limited water exchange occurring only through its southern connection to the South Yellow Sea (Fig. 1). Eleven seasonal rivers, including the Dagu River, Licun River, and Moshui River, discharge into the bay. These rivers exhibit negligible discharge except during heavy summer rainfall events. Notably, eastern coastal rivers such as the Moshui River and Licun River have been transformed into conduits for industrial and domestic wastewater discharges under intensive urbanization pressures.¹⁰ Statistical data indicate that the total volume of municipal wastewater discharged into Jiaozhou Bay increased from $0.846 \times 10^8 \text{ t}$ in 1980 to $5.09 \times 10^8 \text{ t}$ in 2014, with corresponding chemical oxygen demand (COD) and ammonia nitrogen emissions reaching $1.44 \times 10^5 \text{ tonnes}$ and $1.22 \times 10^4 \text{ t}$, respectively.¹¹ Approximately 75% of Qingdao's municipal wastewater is discharged into Jiaozhou Bay.¹² The average water residence time in the bay is 52 days, extending to over 100 days in the western region and decreasing to 40 days near the bay mouth.¹² This prolonged retention of terrestrially derived

pollutants likely amplifies biogeochemical processes within the bay, including aerobic respiration and primary production.

2.2 Resource of pH data

The long-term pH variation data in Jiaozhou Bay were derived from two primary sources: field investigations conducted by our research group and literature-based datasets.

2.2.1 Field investigations. We conducted 33 cruises in Jiaozhou Bay between 2007 and 2016 (Table 1). Each cruise included 13 to 33 sampling stations, with 25 cruises comprising over 30 stations, 6 cruises approximately 25 stations, and only 2 cruises limited to 13 stations. Despite variations in station numbers, the sampling stations were uniformly distributed across the entire bay during each cruise, ensuring that the average pH values represent the bay-wide pH levels (except for February 2014, when instrument failure prevented sampling at six stations near the bay mouth).

For pH measurements, a pH-S-2 pH meter (Ross electrode; accuracy ± 0.02) was used during the November 2007 cruise, while all subsequent cruises employed an Orion 3 Star Benchtop pH meter (Ross electrode; Thermo Fisher Scientific Inc.,

Table 1 Sampling cruises for pH in Jiaozhou Bay from 2007 to 2016

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2007											✓	
2008		✓						✓				
2009			✓									
2010					✓			✓				
2011			✓						✓	✓		✓
2012	✓							✓				
2013				✓	✓							
2014		✓	✓	✓	✓	✓	✓✓ ^a	✓	✓	✓	✓	✓
2015	✓		✓	✓								
2016	✓✓ ^a					✓	✓					

^a Two ✓ indicate that two sampling cruises were conducted this month.

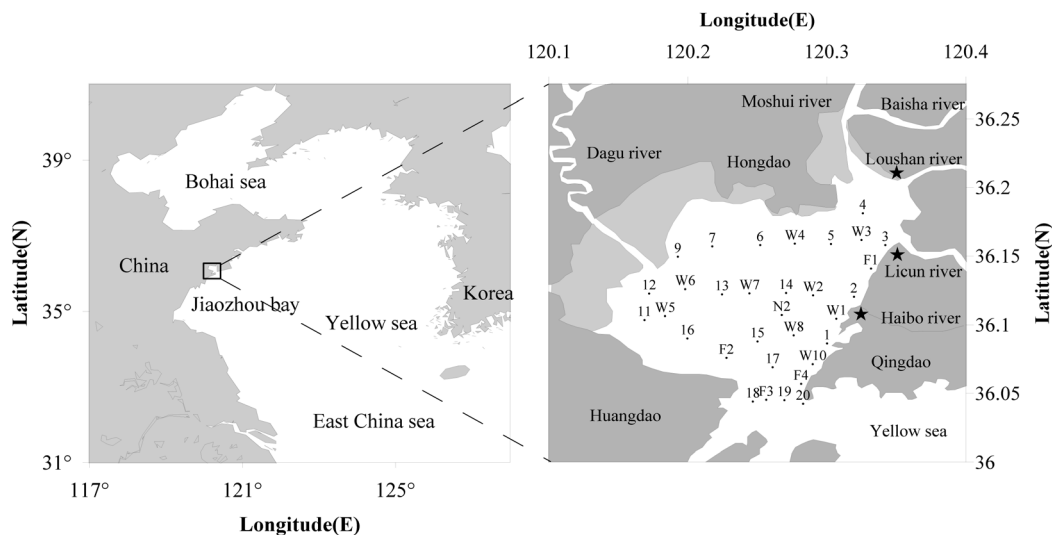


Fig. 1 Sampling stations in Jiaozhou Bay (*i.e.* Jun., 2014 Investigation). Light grey shadow indicates the wetland; the stars indicate Loushan River Wastewater Treatment Plant, Licun River Wastewater Treatment Plant and Haibo River Wastewater Treatment Plant from top to bottom).



Beverly, MA, USA) for *in situ* duplicate measurements. All measurements followed the NBS scale with a precision of ± 0.005 . The consistency in both station distribution and measurement precision ensures comparability of pH datasets across all cruises.

2.2.2 Literature-based data. Since the 1950s, extensive biogeochemical studies have been conducted in Jiaozhou Bay by numerous researchers. The historical pH data utilized in this study were compiled from publicly available datasets published in peer-reviewed journals, dissertations, monographs, and technical reports since 1950. Although the specific electrodes and pH meters employed across these studies varied, all measurements were fundamentally based on electrode potential principles and adhered to the NBS scale recommended by the National Marine Monitoring Standards of China. This methodological consistency ensures comparability among pH datasets derived from diverse literature sources.

However, a critical review of the collected literature on pH studies in Jiaozhou Bay reveals significant inconsistencies in spatial coverage and station configurations across historical datasets. Many investigations did not encompass the entire bay, and variations in sampling design and spatial resolution hinder direct comparability. To address these limitations, this study integrates existing pH datasets by defining a unified study area and applying spatial normalization to harmonize pH measurements obtained at differing spatial scales.

The spatial distribution of seawater pH is governed by dynamic biogeochemical processes, including aerobic respiration, primary production, terrestrial inputs, calcium carbonate precipitation, and air-sea CO₂ exchange. The seasonal dominance of these processes drives cyclical intra-annual variations in pH spatial patterns, while interannual consistency in pH distribution trends during corresponding seasons exhibits statistical significance. This temporal stability ensures that relative pH magnitudes across sub-regions of Jiaozhou Bay remain consistent within the same seasonal period. For instance, Zhang *et al.* documented a northeast-to-mouthward increasing pH gradient in November 2007,³¹ a pattern corroborated by data from November 2014 (unpublished). Leveraging this spatial coherence, pH levels in unmonitored sub-regions can be extrapolated from known values in adjacent areas during synchronous periods.

To address spatial pH correction, this study adapts the Domain-Averaged Concentration Correction Method for Pollutant Heterogeneity in Target Areas proposed by Wang *et al.*³² to the pH of Jiaozhou Bay. Given that pH lacks a direct “concentration” metric, the methodology was modified by first converting pH to H⁺ concentration ([H⁺]), applying corrections, and subsequently reconvert the adjusted [H⁺] back to pH.

Specifically, the study area surveyed by our research group was designated as the reference domain (Fig. 1). For pH datasets from literature, overlapping sub-regions between the literature-reported areas and the reference domain were identified. Domain-averaged [H⁺] values for these overlapping areas were calculated using our reference dataset (*i.e.*, monthly pH measurements from field investigations). The ratio of domain-averaged [H⁺] between the reference domain and overlapping

sub-regions was then derived (eqn (1)). This ratio served as a correction factor to harmonize pH data across spatially inconsistent study areas.

$$\gamma_s = \frac{C_m^i}{C_m^s}, \quad (1)$$

where C_m^i is the average [H⁺] in the overlapping area between the literature-investigated sea area and the reference sea area, and C_m^s is the average [H⁺] in the overlapping area between the reference sea area and the literature-investigated sea area.

Then, by using the regional average [H⁺] of the reference sea area and the aforementioned ratio, the corrected average [H⁺] can be obtained (eqn (2)).

$$C_p^s = C_p^i \times \gamma_s, \quad (2)$$

Where is the current regional average [H⁺] of the reference sea area, and is the corrected regional average [H⁺] of the reference sea area.

The domain-averaged [H⁺] correction enables literature-derived pH data from studies with incomplete spatial coverage of Jiaozhou Bay to better approximate the bay-wide average pH levels. However, this correction method solely accounts for differences in the spatial distribution trends of H⁺ concentrations, neglecting variations in concentration gradients. This limitation may introduce systematic underestimation or overestimation of pH. Nevertheless, spatial pH normalization remains scientifically valuable, as it facilitates the inclusion of heterogeneous datasets into long-term trend analyses, thereby improving the alignment of results with actual pH dynamics.

3. Results

The pH data shown in Fig. 2 represent annual average pH values in Jiaozhou Bay. The pH dataset spanning 1980 to 2016 was

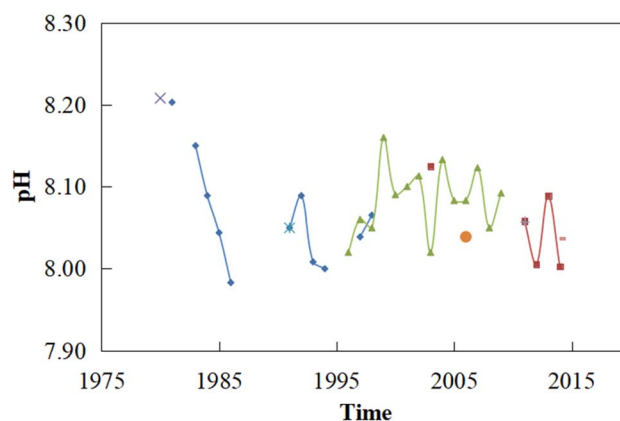


Fig. 2 Long-term variation of pH in Jiaozhou Bay. Note: pH dataset from 1980 to 2016 was composed of multiple sections. The first was from the doctoral dissertations of Zhao¹⁴ (blue rhombus) and Dong¹⁸ (green triangle). The second was from a book named *Evolution of the chemical environment in Jiaozhou Bay* written by Song *et al.*¹⁹ (red square). The third was from our research group (pink red stripes). The last was from various literature (purple times sign,¹³ blue times sign,¹⁷ orange circle,²³ light blue cross²⁷).



Table 2 Sampling cruises for pH in Jiaozhou Bay from 2007 to 2016

Data source	Sampling period	Analytical methods and standards	Study area	Number of stations
Diao, 1984 (ref. 13)	May, August, November 1980; February 1981	Not specified	Cross-shaped distribution	10
Zhao, 2002 (ref. 14)	1981; 1983–1986; 1992–1994; 1998	Not specified	Entire bay	N/A
China bay records, vol. 4 (ref. 15)	January, May, September 1986	Not specified	Entire bay	N/A
Ji <i>et al.</i> , 1993 (ref. 16)	October 1989	pHS-2 pH meter	Entire bay (excluding mouth)	23
Shen and Liu., 1997 (ref. 17)	August, November 1991; February, May 1992	pH D-1 pH meter	Entire bay	10
Dong, 2011 (ref. 18)	1996–2009	Glass electrode method	Entire bay	N/A
Song <i>et al.</i> , 2016 (ref. 19)	2002; 2011–2014	Not specified	Entire bay	N/A
Li <i>et al.</i> , 2007 (ref. 20)	June, July, November 2003; February 2004	ORION 420A + pH meter	Entire bay	22
Wei and Xue, 2004 (ref. 21)	October–November 2003	National standard GB3097-1997 (seawater quality standards)	Hongdao coastal area	17
Dang <i>et al.</i> , 2008 (ref. 22)	September–October 2004	Multi-parameter analyzer	Entire bay	10
Zhong, 2010 (ref. 23)	August, December 2006; April, October 2007	pH meter method	Central and mouth areas	7
Jiang <i>et al.</i> , 2012 (ref. 24)	June 2007 to May 2008	Multi-parameter water quality analyzer (MS5, HACH)	Entire bay	5
Deng <i>et al.</i> , 2016 (ref. 25)	August, November 2007; January 2008; April 2010	Fisher pH meter (AR15) with Ross-8102 pH electrode	Entire bay	18
Zhai <i>et al.</i> , 2014 (ref. 26)	February, May, August, November 2011	Marine monitoring protocols	Central and mouth areas	12
Liu <i>et al.</i> , 2013 (ref. 27)	September–November 2011	Electrode potentiometry and spectrophotometry	Entire bay	15
Zhou, 2013 (ref. 28)	May 2012	Spectrophotometry calibrated to electrode potentiometry	Entire bay	15
Wang, 2013 (ref. 29)	July–August 2012	Multi-parameter water quality analyzer	Entire bay	23
Liu, 2012 (ref. 30)	September 2012–August 2013	pH meter method (accumet AR15, Fisher Scientific, Pittsburgh, PA)	Entire bay	15

compiled from four primary sources: the PhD dissertations of Zhao¹⁴ and Dong,¹⁸ the book Chemical Environmental Evolution of Jiaozhou Bay by Song *et al.*¹⁹ Data collected by our research group in 2014, and annual (or at least seasonal) pH surveys or reports from other literature (Table 2). Despite the diverse sources, the pH data from different studies are comparable. For overlapping months, minor differences were observed between datasets. For example, the pH values reported by Diao for 1980 (ref. 13) and Zhao for 1981 (ref. 14) both exhibited relatively high levels, confirming elevated pH conditions during that period. Similarly, overlapping data from Zhao¹⁴ and Dong¹⁸ for 1997 and 1998 showed consistent pH levels.

As shown in Fig. 2, Jiaozhou Bay exhibited significant interannual pH fluctuations from 1980 to 2016, with a maximum variation of 0.23. Overall, pH displayed a declining trend with a rate of 0.0062 years⁻¹, which is 3.6 times faster than that reported in the open oceans (~0.0017 years⁻¹), indicating pronounced anthropogenic impacts on pH in the bay. The decrease in pH in Jiaozhou Bay does not follow a continuous

downward trend as observed in the open ocean. Instead, it exhibited three distinct phases of change: a gradual decrease from 1980 to 1986, followed by a gradual increase from 1986 to 2004, and then a renewed downward trend from 2004 to 2016. Regression analysis of these phases yielded pH change rates of -0.0389 years⁻¹, 0.0081 years⁻¹, and -0.0089 years⁻¹, respectively (Fig. 3). Notably, the pH decline rates during the first and third phases were 23 times and 5 times higher, respectively, than those in the open ocean.

4. Discussion

4.1 Controlling effects of untreated wastewater on pH decline from 1980 to 1986

From 1980 to 1986, the pH in Jiaozhou Bay decreased by 0.23 units over just six years (Fig. 2). Based on long-term temperature variations in the bay (Fig. 4a), seawater temperature increased by approximately 1.6 °C from 1981 to 1985. Gieskes proposed that a 1 °C change in temperature alters seawater pH by 0.0114 units.³³ If only considering thermodynamic effects, the 1.6 °C



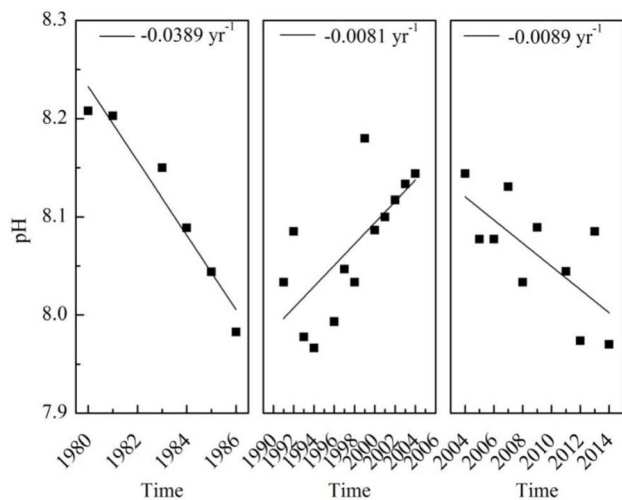


Fig. 3 Linear regression of pH data from different time periods in Jiaozhou Bay (for overlapping data points within the same year, data that better align with the variation patterns of adjacent years were selected for fitting).

temperature rise from 1981 to 1985 would account for a pH decrease of approximately 0.02 units. However, the observed pH decline during this period was 0.16 units, indicating that temperature rise was not the primary driver of the pH reduction.

Notably, during 1980 to 1986, dissolved oxygen (DO) levels in Jiaozhou Bay were relatively low with DO in 1981 only 6.1 mg L^{-1} , which equivalent to $\sim 71\%$ saturation. Meanwhile, NH_4^+ concentrations nearly doubled, NO_2^- and NO_3^- remained stable (Fig. 4c–f), and $\text{PO}_4\text{-P}$ decreased by about half (Fig. 4h). First, the significantly undersaturated DO levels ($\sim 71\%$) suggested poor seawater quality during this period, likely due to substantial organic matter input and subsequent degradation, releasing CO_2 and lowering pH. Second, elevated NH_4^+ concentrations, rising temperatures, and low DO levels collectively enhanced nitrification. Nitrification releases 2 moles of H^+ per mole of NH_4^+ oxidized, significantly reducing seawater pH. Third, although increased dissolved inorganic nitrogen (DIN) concentrations (primarily NH_4^+) could theoretically support phytoplankton primary production by providing nitrogen nutrients, the rising DIN/ $\text{PO}_4\text{-P}$ ratio (reaching 22 by 1986, significantly higher than the Redfield ratio of 16 (ref. 34)) likely led to phosphorus limitation, suppressing primary productivity. The same phenomenon has been observed in Sagami Bay of Japan,³⁵ the northwestern Mediterranean coastal area (Lion's Gulf),³⁶ and Moreton Bay in Australia.³⁷

Thus, the sharp pH decline in Jiaozhou Bay from 1980 to 1986 was likely driven by intensified aerobic respiration, enhanced nitrification, and reduced primary production.

The environmental degradation observed in Jiaozhou Bay between 1980 and 1986 may be closely related to the rapid expansion of the light textile industry in Qingdao City. Qingdao has a long-standing history of textile production, with its industrial structure predominantly focused on light textiles since the early 20th century. Following China's reform and opening-up policy in 1978, the textile sector in Qingdao

experienced swift growth by adopting advanced foreign technologies.³⁸ By 1987, light textiles accounted for 60.5% of the total industrial output in Qingdao. The textile industry's development led to massive discharges of wastewater rich in organic matter and NH_4^+ into Jiaozhou Bay, with a large portion directly discharged into the bay untreated. This likely contributed to the notable decline in pH during this period.

4.2 Controlling effects of wastewater treatment and nutrient input on pH increase from 1991 to 2004

From 1991 to 2004, the pH in Jiaozhou Bay showed an upward trend with an increase of approximately 0.1 units (Fig. 2). During this period, seawater temperature generally declined (Fig. 4a), but the maximum temperature drop of $\sim 0.7 \text{ }^\circ\text{C}$ would account for a pH increase of less than 0.01 units based on thermodynamic principles, indicating that temperature was not the primary driver of the pH rise. As shown in Fig. 4c, DO levels in Jiaozhou Bay significantly increased after 1994. In 1994, DO was only 6.4 mg L^{-1} (equivalent to 76% saturation under the prevailing salinity and temperature conditions: $S = 31.93$, $T = 14.33$), reflecting a markedly undersaturated state. By 2004, DO levels reached full saturation. This transition from undersaturation to saturation likely resulted from reduced aerobic respiration and/or enhanced primary production.

The observed pH increase may also be linked to reduced organic pollutant inputs. From 1993 to 1999, four large-scale wastewater treatment plants were constructed and operationalized around Jiaozhou Bay,⁴¹ significantly improving wastewater treatment rates. According to the Qingdao Environmental Status Bulletin, municipal wastewater treatment rates increased from 34.9% to 59.5%, and industrial wastewater treatment rates rose from 86.6% to 99.1% between 1998 and 2004 (Fig. 5c).⁴² Concurrently, COD discharges decreased: municipal COD emissions dropped from 49 400 tons to 39 800 tons, and industrial COD emissions declined from 35 300 tons to 16 000 tons during the same period (Fig. 5b). Wastewater treatment preferentially removes readily degradable organic matter, leaving less bioavailable organic compounds in discharged effluents. This reduction in both the quantity and degradability of organic inputs likely weakened aerobic respiration in the bay, contributing to the pH rise.

Enhanced primary production may also have driven the pH increase. From 1994 to 2004, DIN concentrations more than doubled (Fig. 4g), while $\text{PO}_4\text{-P}$ and silicate ($\text{SiO}_3\text{-Si}$) levels increased 3–4 times (Fig. 4h–i). These nutrient surges shifted the bay from an oligotrophic state (thresholds: $\text{DIN} = 0.2 \text{ mg L}^{-1}$, $\text{PO}_4\text{-P} = 0.01 \text{ mg L}^{-1}$ (ref. 43)) to a mesotrophic state (thresholds: $\text{DIN} = 0.3 \text{ mg L}^{-1}$, $\text{PO}_4\text{-P} = 0.02 \text{ mg L}^{-1}$ (ref. 43)). Furthermore, as indicated by the different increase rates of DIN, $\text{PO}_4\text{-P}$, and $\text{SiO}_3\text{-Si}$, the DIN/ $\text{PO}_4\text{-P}$ and DIN/ $\text{SiO}_3\text{-Si}$ ratios in Jiaozhou Bay have gradually decreased. The DIN/ $\text{PO}_4\text{-P}$ ratio declined progressively from 73 in 1994 to 29 in 2004, while the DIN/ $\text{SiO}_3\text{-Si}$ ratio decreased from approximately 16 in 1995 to around 2 in 2004. These changes have led to a gradual weakening of the limiting effects of $\text{PO}_4\text{-P}$ and $\text{SiO}_3\text{-Si}$ on phytoplankton primary production. The combined effects of nutrient enrichment and



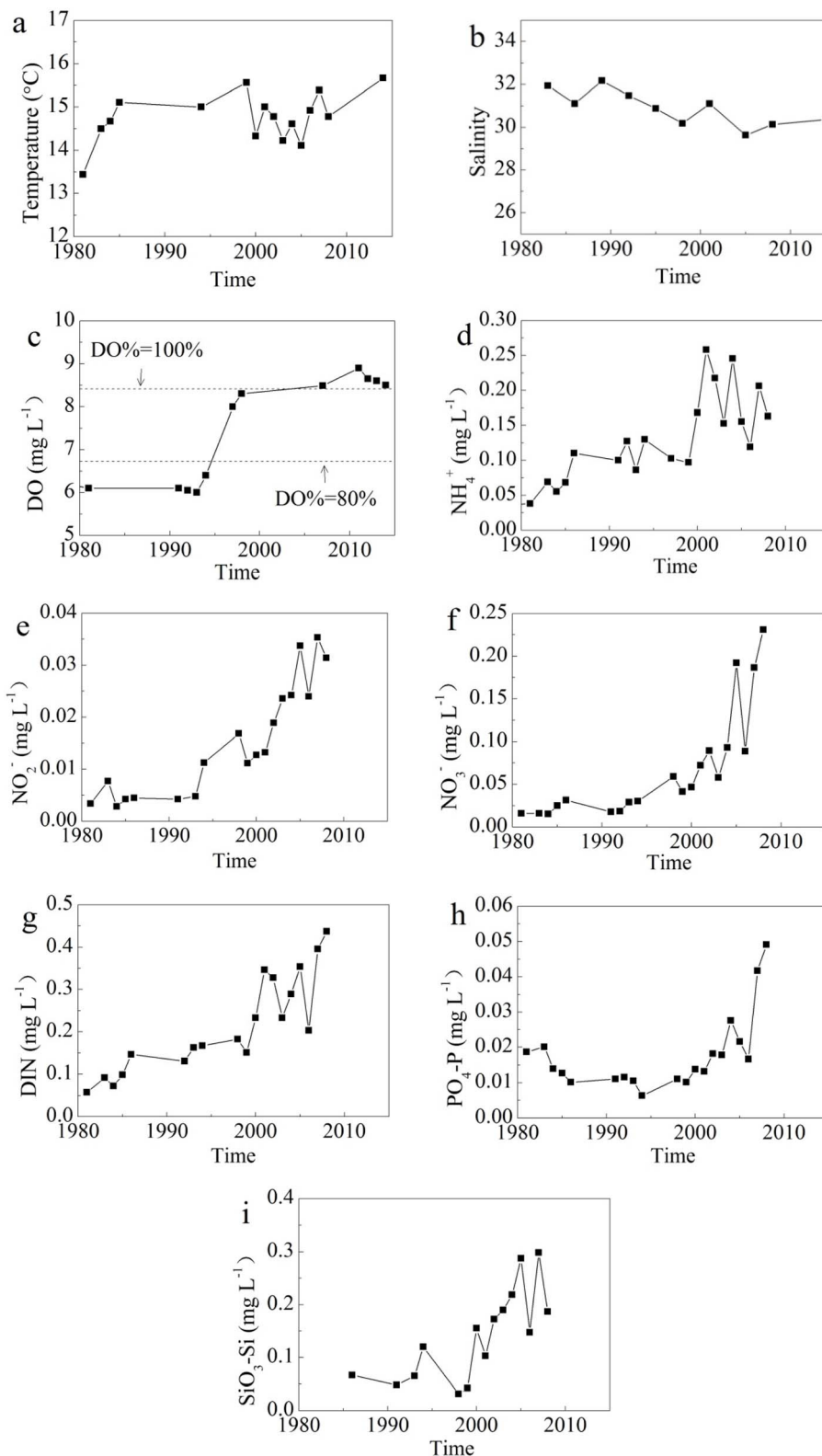


Fig. 4 Long-term variation of parameters in Jiaozhou Bay. Seawater temperature (a), salinity (b), data sources: Sun *et al.*, 2011,³⁹ and the 2014 data were determined by our research group. DO (c), data sources: Song *et al.*, 2016 (1991–2014);¹⁹ Jiang *et al.*, 2012 (2007).²⁴ NH₄⁺ (d), NO₂⁻ (e), NO₃⁻ (f), DIN (g), PO₄-P (h), SiO₃-Si (i), data sources: Sun *et al.*, 2011.⁴⁰



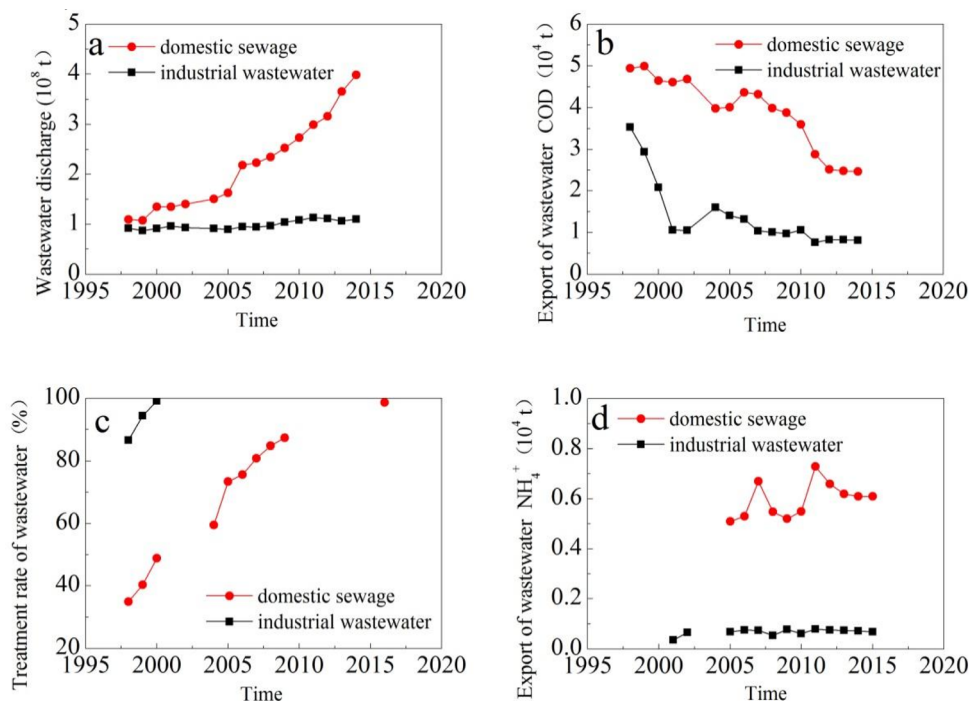


Fig. 5 Long-term variation of emissions of industrial wastewater and domestic sewage (a), emissions of COD (b), treatment rates (c) and emissions of NH_4^+ (d). (Data sources: Qingdao Environmental Protection Bureau, 1999–2014).³⁶

balanced stoichiometry likely stimulated primary production, elevating pH through photosynthetic CO_2 uptake.

The nutrient regime shift in Jiaozhou Bay during this period may also relate to increased municipal wastewater discharges (Fig. 5). While industrial wastewater volumes remained stable from 1998 to 2004, municipal sewage discharges surged by ~ 1.4 times (Fig. 5a). Municipal wastewater typically contains ~ 8 times more NH_4^+ than industrial effluents (Fig. 5d), explaining the observed ammonium increases. Although $\text{PO}_4\text{-P}$ data for municipal wastewater are unavailable, phosphorus-rich detergents in household sewage likely drove the rapid $\text{PO}_4\text{-P}$ rise.

4.3 Controlling effects of eutrophication and direct discharge of high-DIC treated sewage on pH decline from 2004 to 2016

Since 2004, seawater pH in Jiaozhou Bay had exhibited a gradual downward trend, decreasing by approximately 0.1 units over a decade (Fig. 2). While seawater temperature generally rose during this period with a maximum increase of 1.6 °C (Fig. 4a), the associated thermodynamic effect would account for only ~ 0.02 units of pH decline, indicating minimal contribution from temperature changes.

By 2004, the bay had reached a mesotrophic state. By 2007, DIN concentrations exceeded 0.4 mg L^{-1} and $\text{PO}_4\text{-P}$ surpassed 0.03 mg L^{-1} (Fig. 4g and h), transitioning the system to a eutrophic state.⁴⁴ Eutrophication promoted massive phytoplankton blooms that initially absorb atmospheric CO_2 for organic carbon storage. However, during bloom senescence, this stored carbon was degraded *via* aerobic respiration, releasing CO_2 back into seawater and lowering pH.

Additionally, wastewater discharge patterns during 2004 to 2008 likely contributed to the pH decline (Fig. 5). In 2004, municipal and industrial wastewater discharges were comparable (Fig. 5a). Rapid urbanization and population growth subsequently drove a ~ 3.6 -fold increase in municipal sewage relative to industrial effluents by 2014 (Fig. 5a). Notably, while municipal sewage discharges increased, the COD emissions exhibited a gradual decline, likely attributable to improved wastewater treatment rates. Although data on urban sewage treatment rate in Qingdao was limited, existing data indicated an upward trend in domestic sewage treatment rates over the years (Fig. 5c). The sewage treatment rate in 2004 was just 59.5%, but by 2016 it had risen to 98.6%. This meant most sewage entering Jiaozhou Bay was treated to remove organic matter. Alshboul *et al.* demonstrated that wastewater treatment plants (WWTPs) typically remove $>98\%$ of organic carbon, shifting carbon exports toward DIC.⁴⁴ The TALK: DIC in sewage was typically close to 1,⁴⁵ lower than that in Jiaozhou Bay, which had an annual average ratio of 1.10. TALK consists mainly of HCO_3^- and CO_3^{2-} , while DIC includes HCO_3^- , CO_3^{2-} , and CO_2 . HCO_3^- and CO_3^{2-} are alkaline, whereas CO_2 is acidic. A decrease in the TALK: DIC ratio indicates either a reduction in HCO_3^- and CO_3^{2-} or an increase in CO_2 —both of which can lead to a decline in seawater pH. Therefore, the long-term discharge of wastewater may be a key factor contributing to the decrease in pH observed in Jiaozhou Bay during this period. Thus, the formation of eutrophic seawater in the bay and the direct discharge of high-DIC treated sewage were likely the main reasons for the pH decline from 2004 to 2016.



Over the 36 year study period (1980–2016), anthropogenic impacts had dominantly shaped pH dynamics in Jiaozhou Bay. Mirroring patterns in developed regions, Qingdao experienced initial environmental degradation (pH decline) during rapid industrialization, followed by partial recovery (pH rise) through pollution control measures. Future wastewater management strategies must expand beyond organic matter and nutrient removal to address pH-lowering effects of DIC in treated effluents.

5. Conclusions

From 1980 to 2016, the pH in Jiaozhou Bay declined at a rate of 0.0062 units per year, which is 3.6 times faster than that in the open oceans. Unlike the persistent downward trend in the open oceans, the pH dynamics in Jiaozhou Bay followed three distinct phases: a decrease from 1980 to 1986, an increase from 1991 to 2004, and a renewed decline from 2004 to 2016.

Analysis of DO, NH_4^+ , and $\text{PO}_4\text{-P}$ variations suggested that the 1980–1986 pH decline was driven by intensified aerobic respiration, enhanced nitrification, and reduced primary production. These shifts likely stemmed from untreated textile industry wastewater discharges linked to Qingdao's rapid industrial growth post-reform and opening-up. The 1986–2004 pH increase correlated with reduced organic inputs (due to improved wastewater treatment), alongside nutrient enrichment (NH_4^+ , $\text{PO}_4\text{-P}$) and balanced DIN/ $\text{PO}_4\text{-P}$ and DIN/ $\text{SiO}_3\text{-Si}$ ratios, which alleviated nutrient limitations and stimulated primary production. Conversely, the 2004–2016 pH decline coincided with eutrophication-induced CO_2 release from organic matter degradation and direct discharge of DIC from treated effluents. Based on changes in COD and DIC emissions from wastewater treatment plants, as well as variations in seawater NH_4^+ and $\text{PO}_4\text{-P}$ concentrations, the eutrophication of Jiaozhou Bay and the direct discharge of DIC-rich effluents likely constituted the primary drivers of the pH decline observed between 2004 and 2016.

Human activities, particularly wastewater discharges, have profoundly shaped Jiaozhou Bay's pH trajectory. Future management strategies must address not only organic and nutrient removal but also mitigate the pH-lowering effects of DIC in treated effluents to safeguard coastal carbonate chemistry.

Author contributions

Conceptualization, J. W. and P. H.; methodology, P. H.; software, P. H.; validation, J. W.; formal analysis, P. H.; investigation, P. H.; resources, J. W.; data curation, P. H.; writing – original draft preparation, P. H.; writing – review and editing, J. W. and P. H.; visualization, P. H.; funding acquisition, F. C. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

CO_2	carbon dioxide
DIC	dissolved inorganic carbon
COD	chemical oxygen demand
DO	dissolved oxygen
DIN	dissolved inorganic nitrogen
WWTPs	wastewater treatment plants

Data availability

Requests for data that support the findings of this study can be sent hanping900304@163.com.

Acknowledgements

This work was supported by the Financial support for scientific research projects of Hainan flexible talent introduction and innovation platform and the Research Project of the Academician Innovation Platform of Hainan Province (YSPTZX202149).

References

- 1 G. A. Florides and P. Christodoulides, Global warming and carbon dioxide through sciences, *Environ. Int.*, 2009, **35**(2), 390–401.
- 2 P. N. Pearson and M. R. Palmer, Atmospheric carbon dioxide concentrations over the past 60 million years, *Nature*, 2000, **406**(6797), 695–699.
- 3 J. M. Santana-Casiano, M. González-Dávila, M. J. Rueda, *et al.*, The interannual variability of oceanic CO_2 parameters in the northeast Atlantic subtropical gyre at the ESTOC site, *Global Biogeochem. Cycles*, 2007, **21**(GB1015), 1–16.
- 4 N. R. Bates, Interannual variability of the oceanic CO_2 sink in the subtropical gyre of the North Atlantic Ocean over the last 2 decades, *J. Geophys. Res. C Oceans*, 2007, **112**(C09013), 1–26.
- 5 J. E. Dore, R. Lukas, D. W. Sadler, *et al.*, Physical and biogeochemical modulation of ocean acidification in the central North Pacific, *Proc. Natl. Acad. Sci.*, 2009, **106**(30), 12235–12240.
- 6 J. C. Orr, V. J. Fabry, O. Aumont, *et al.*, Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, *Nature*, 2005, **437**(7059), 681–686.
- 7 J. T. Wootton, C. A. Pfister and J. D. Forester, Dynamic patterns and ecological impacts of declining ocean pH in a high-resolution multi-year dataset, *Proc. Natl. Acad. Sci.*, 2008, **105**(48), 18848–18853.
- 8 A. Brutemark, J. Engström-Öst and A. Vehmaa, Long-term monitoring data reveal pH dynamics, trends and variability in the western Gulf of Finland, *Oceanol. Hydrobiol. Stud.*, 2011, **40**(3), 91–94.
- 9 P. Provoost, S. Van Heuven, K. Soetaert, *et al.*, Seasonal and long-term changes in pH in the Dutch coastal zone, *Biogeochemistry*, 2010, **7**(11), 3869–3878.



- 10 Z. Gao, D. Yang, J. Qin, *et al.*, The land-sourced pollution in the Jiaozhou Bay, *Chin. J. Oceanol. Limnol.*, 2008, **26**(2), 229–232.
- 11 Qingdao Municipal Environmental Protection Bureau, *2014 Report on the Environmental Status of Qingdao*, 2015.
- 12 Z. Liu, H. Wei, G. Liu, *et al.*, Simulation of water exchange in Jiaozhou Bay by average residence time approach, *Estuarine, Coastal Shelf Sci.*, 2004, **61**(1), 25–35.
- 13 D. Huanxiang, A relative study on the relation between phytoplankton and inorganic environment in Jiaozhou Bay, *Mar. Sci.*, 1984, **4**, 16–19.
- 14 Z. Shujiang, *Long-term Changes of Main Ecological Factors of the Jiaozhou Bay Ecosystem*, Institute of Oceanology, Chinese Academy of Sciences, Qingdao, 2002.
- 15 W. Wang, D. Xia and X. Gao, *China Bay Records*, Ocean Press, Beijing, 1993, Vol. 4.
- 16 R. Ji, G. Chen, L. Zhang, *et al.*, The density of water in Jiaozhou Bay, *Acta Oceanol. Sin.*, 1993, **15**(5), 136–141.
- 17 S. Zhiliang and L. Mingxing, Research on Carbon Dioxide in the Coastal Sea Water of Jiaozhou Bay, *Acta Oceanol. Sin.*, 1997, **19**(2), 115–120.
- 18 Z. Dong, *Jiaozhou Bay Water Environmental Quality Assessment and Pollution Control*, Ocean University of China, Qingdao, 2011.
- 19 J. Song, L. Duan and H. Yuan, *Evolution of the Chemical Environment in Jiaozhou Bay*, Science Press, Beijing, 2016.
- 20 X. Li, N. Li, X. Gao, *et al.*, Dissolved inorganic carbon and CO₂ fluxes across Jiaozhou Bay air-water interface, *Acta Oceanol. Sin.*, 2004, **23**(2), 279–285.
- 21 Y. Wei and J. Xue, Preliminary research of current environmental situation of sea water in Hongdao area of Jiaozhou Bay in 2003, *Mar. Sci.*, 2004, **28**(9), 75–77.
- 22 H. Dang, J. Ren, L. Song, *et al.*, Diverse tetracycline resistant bacteria and resistance genes from coastal waters of Jiaozhou Bay, *Microb. Ecol.*, 2008, **55**(2), 237–246.
- 23 M. Zhong, *Ecosystem Health Assessment of Jiaozhou Bay*, Ocean University of China, Qingdao, 2010.
- 24 Y. Jiang, H. Xu, X. Hu, *et al.*, An approach to analyzing spatial patterns of planktonic ciliate communities for monitoring water quality in Jiaozhou Bay, northern China, *Mar. Pollut. Bull.*, 2011, **62**(2), 227–235.
- 25 X. Deng, Y. Hu, C. Liu, *et al.*, Distribution and seasonal variations of carbonate system in the Jiaozhou Bay, China, *Oceanol. Limnol. Sinica*, 2016, **47**(1), 234–244.
- 26 L. Zhai, D. Han, D. Fu, *et al.*, Fish community structure and the relationship with environmental factors in Jiaozhou Bay and adjacent waters, *J. Fish. Sci. China*, 2014, **21**(4), 810–821.
- 27 S. Liu, C. Liu, P. Yan, *et al.*, Research of spectrophotometric pH measurements of seawaters in Jiaozhou Bay and coastal waters of Qingdao, *Trans. Oceanol. Limnol.*, 2013, (3), 108–114.
- 28 Y. Zhou, *Studying of Effects of Low-Molecular-Weight Organic Acids on pH of Seawater in the Jiaozhou Bay*, Ocean University of China, Qingdao, 2013.
- 29 W. Wang, *The Influence of Typhoon-Induced Precipitation on the Supplementary of Biogenic Elements, the Abundance and Structure of Phytoplankton in Jiaozhou Bay*, Ocean University of China, Qingdao, 2013.
- 30 Z. Liu, *Studying on Characteristics of Low Molecular-Weight Organic Acids in the Surface Water of the Jiaozhou Bay*, Ocean University of China, Qingdao, 2012.
- 31 L. Zhang, M. Xue and Q. Liu, Distribution and seasonal variation in the partial pressure of CO₂ during autumn and winter in Jiaozhou Bay, a region of high urbanization, *Mar. Pollut. Bull.*, 2012, **64**(1), 56–65.
- 32 C. Wang, X. Wang, S. Liang, *et al.*, The methods for calibrating average concentration in the domain and estimating average annual concentration of pollutants in the sea area being partially or totally different from target domains, *Acta Oceanol. Sin.*, 2010, **32**(2), 155–160.
- 33 J. M. Gieskes, Effect of temperature on the pH of seawater, *Limnol. Oceanogr.*, 1969, **14**(5), 679–685.
- 34 A. C. Redfield, B. H. Ketchum and F. A. Richards, The influence of organisms on the composition of seawater, *The Sea*, 1963, vol. 2, pp. 26–77.
- 35 T. Fujiki, T. Toda, T. Kikuchi, *et al.*, Phosphorus limitation of primary productivity during the spring-summer blooms in Sagami Bay, Japan, *Mar. Ecol.: Prog. Ser.*, 2004, **283**, 29–38.
- 36 F. Diaz, P. Raimbault, B. Boudjellal, *et al.*, Early spring phosphorus limitation of primary productivity in a NW Mediterranean coastal zone (Gulf of Lions), *Mar. Ecol.: Prog. Ser.*, 2001, **211**, 51–62.
- 37 F. Wulff, B. D. Eyre and R. Johnstone, Nitrogen versus phosphorus limitation in a subtropical coastal embayment (Moreton Bay; Australia): Implications for management, *Ecol. Model.*, 2011, **222**(1), 120–130.
- 38 Qingdao Municipal Ecol. Modell. Office of Local Chronicles, *Qingdao Municipal Chronicles: Textile Industry Annals*, Xinhua Press, Beijing, 1999.
- 39 S. Sun, X. Sun, G. Zhang, *et al.*, Long-term changes in major meteorological and hydrological and factors in the Jiaozhou Bay, *Oceanol. Limnol. Sinica*, 2011, **42**(5), 632–638.
- 40 X. Sun, S. Sun, Z. Zhao, *et al.*, Long-term changes in nutrient concentration and structure in the Jiaozhou Bay, *Oceanol. Limnol. Sinica*, 2011, **42**(5), 662–669.
- 41 L. Yue, H. Gao, M. Liu, *et al.*, The relationships between environment and economy of Qingdao City by using water quality parameters in Jiaozhou Bay, *Mar. Environ. Sci.*, 2016, **35**(1), 106–112.
- 42 Qingdao Municipal Environmental Protection Bureau, *2004–2014 and 2016 Report on the Environmental Status of Qingdao. 2005–2015*, 2017.
- 43 H. Ma, X. Shi, H. Tang, *et al.*, The two-grade set pair analysis method for seawater eutrophication assessment, *Period. Ocean Univ. China*, 2013, **43**(6), 64–70.
- 44 Z. Alshboul, J. Encinas-Fernández, H. Hofmann, *et al.*, Export of dissolved methane and carbon dioxide with effluents from municipal wastewater treatment plants, *Environ. Sci. Technol.*, 2016, **50**(11), 5555–5563.
- 45 X. Yang, L. Xue, Y. Li, *et al.*, Treated Wastewater Changes the Export of Dissolved Inorganic Carbon and Its Isotopic Composition and Leads to Acidification in Coastal Oceans, *Environ. Sci. Technol.*, 2018, **52**(10), 5590.

