PAPER

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

Ping Han,[abc] Jin Wang [ID] *[cde] and Feiyong Chen[de]

Due to anthropogenic carbon dioxide (CO_2) 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.

1. Introduction

The absorption of anthropogenic atmospheric CO_2 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 CO_2 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°57′–36°18 ′N, 120°04′–120°23 ′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 0.846×10^8 t in 1980 to 5.09×10^8 t in 2014, with corresponding chemical oxygen demand (COD) and ammonia nitrogen emissions reaching 1.44×10^5 tonnes and 1.22×10^4 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 pHS-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.
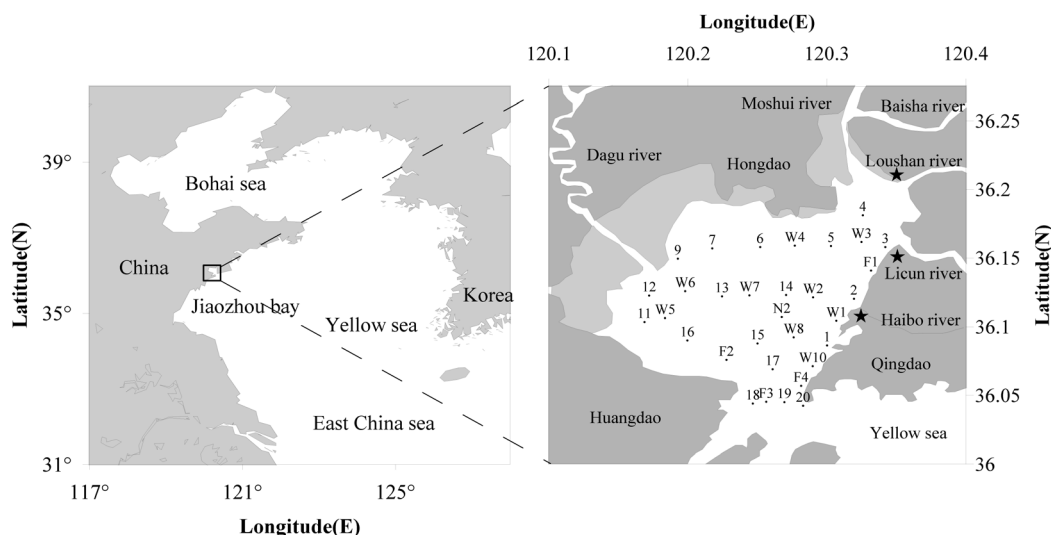

Fig. 1 Sampling stations in Jiaozhou Bay (*i.e.* Jun., 2014 Investigation. Light grey shadow indicates the wetland; the stars indicate Loushan River Wastewater Treatment Plant, Licun River Wastewater Treatment Plant and Haibo River Wastewater Treatment Plant from top to bottom).

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 et al., 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 et al., 2016 (ref. 19)	2002; 2011–2014	Not specified	Entire bay	N/A
Li et al., 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 et al., 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 et al., 2012 (ref. 24)	June 2007 to May 2008	Multi-parameter water quality analyzer (MS5, HACH)	Entire bay	5
Deng et al., 2016 (ref. 25)	August, November 2007; January 2008; April 2010	Fisher pH meter (AR15) with Ross-8102 pH electrode	Entire bay	18
Zhai et al., 2014 (ref. 26)	February, May, August, November 2011	Marine monitoring protocols	Central and mouth areas	12
Liu et al., 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 Zhao[14] 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 Zhao[14] and Dong[18] 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 ($\sim$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
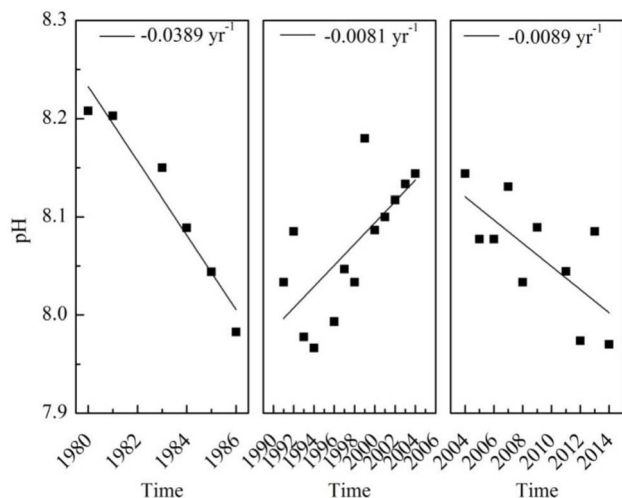
Fig. 3 Linear regression of pH data from different time periods in Jiaozhou Bay (for overlapping data points within the same year, data that better align with the variation patterns of adjacent years were selected for fitting).

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 ~71% saturation. Meanwhile, NH_4^+ concentrations nearly doubled, NO_2^- and NO_3^- remained stable (Fig. 4c–f), and PO_4–P decreased by about half (Fig. 4h). First, the significantly undersaturated DO levels (~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/PO_4–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 ~0.7 °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 PO_4–P and silicate (SiO$_3$–Si) levels increased 3–4 times (Fig. 4h–i). These nutrient surges shifted the bay from an oligotrophic state (thresholds: DIN = 0.2 mg L^{-1}, PO_4–P = 0.01 mg L^{-1} (ref. 43)) to a mesotrophic state (thresholds: DIN = 0.3 mg L^{-1}, PO_4–P = 0.02 mg L^{-1} (ref. 43)). Furthermore, as indicated by the different increase rates of DIN, PO_4–P, and SiO$_3$–Si, the DIN/PO_4–P and DIN/SiO$_3$–Si ratios in Jiaozhou Bay have gradually decreased. The DIN/PO_4–P ratio declined progressively from 73 in 1994 to 29 in 2004, while the DIN/SiO$_3$–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 PO_4–P and SiO$_3$–Si on phytoplankton primary production. The combined effects of nutrient enrichment and

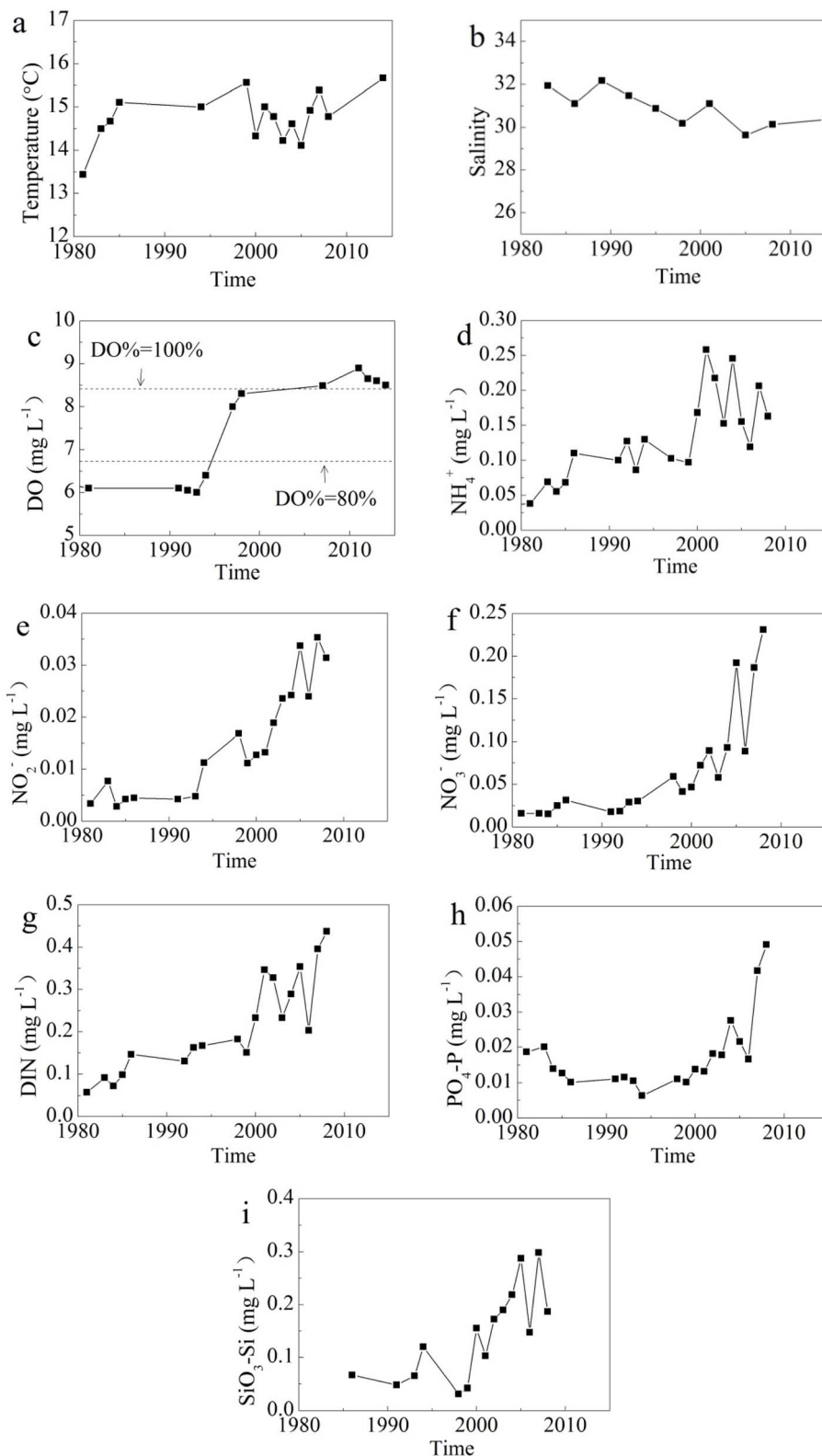Fig. 4   Long-term variation of parameters in Jiaozhou Bay. Seawater temperature (a), salinity (b), data sources: Sun et al., 2011,[39] and the 2014 data were determined by our research group. DO (c), data sources: Song et al., 2016 (1991–2014);[19] Jiang et al., 2012 (2007).[24] NH_4^+ (d), NO_2^- (e), NO_3^- (f), DIN (g), PO_4–P (h), SiO_3–Si (i), data sources: Sun et al., 2011.[40]
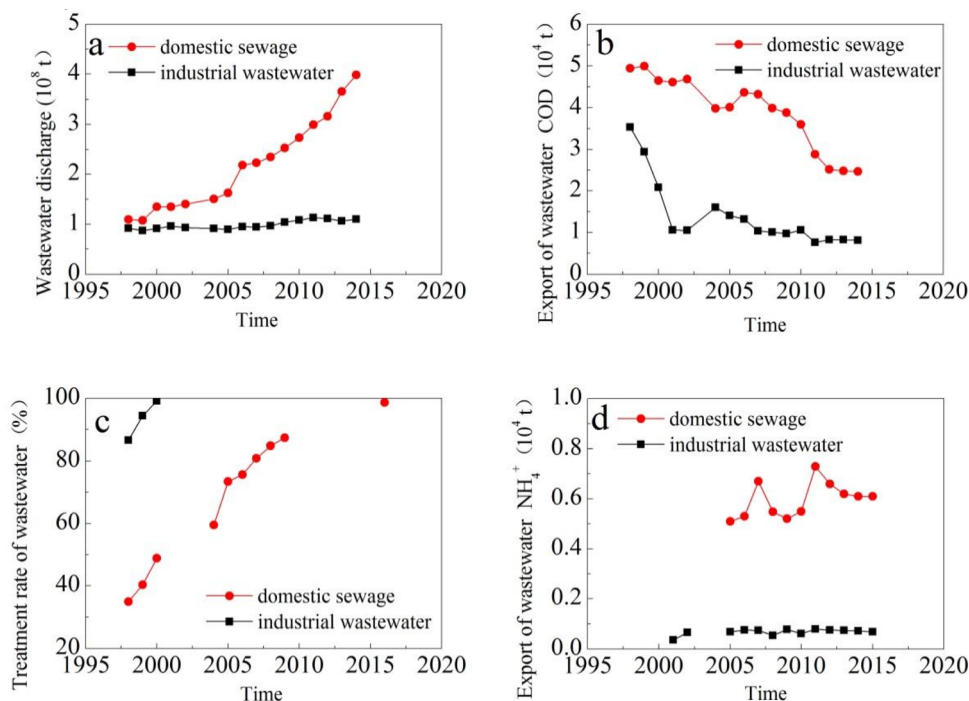
Fig. 5 Long-term variation of emissions of industrial wastewater and domestic sewage (a), emissions of COD (b), treatment rates (c) and emissions of NH_4^+ (d). (Data sources: Qingdao Environmental Protection Bureau, 1999–2014).[36]

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 PO_4–P data for municipal wastewater are unavailable, phosphorus-rich detergents in household sewage likely drove the rapid PO_4–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 PO_4–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 PO_4–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^+, PO_4–P) and balanced DIN/PO_4–P and DIN/SiO_3–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 PO_4–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

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