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Evaluation of spatial variation and nutritional status of environmental quality in the surface seawater from fishing harbours of Hainan island

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Abstract. To investigate the nutrient distribution characteristics and the eutrophication status of the main fishing ports in Hainan Province, this study analyzed the 2021 seawater quality indicators, including biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), chlorophyll a (Chl a), ammonia nitrogen (NH_4-N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N), and soluble active phosphate (DIP). The single-factor contaminant index method was employed to evaluate the water quality, revealing that the levels of COD, BOD_5, and DIP surpass the national seawater quality standards for Type IV. The eutrophication index (EI) of the different fishing ports ranges from 2.38 to 56.29, indicating a high level of eutrophication.

1 Introduction

Fishing ports serve as critical infrastructure for the safe production of fisheries, as well as key bases and hubs for the development of marine biological resources. However, most fishing ports were constructed quite early and generally suffer from weak infrastructure, low construction standards, chaotic management, severe water pollution, and poor environmental conditions [1]. Fishing ports are typically characterized by strong enclosure and low water exchange capacity, making their ecosystems extremely fragile. As coastal cities develop economically, fishing ports become densely populated and experience intense human activity. This leads to the excessive transfer of nutrients into nearshore waters, resulting in severe eutrophication in some coastal areas [2]. Additionally, fishing ports are vital locations for docking fishing boats, loading and unloading cargo, supplying oil and water, processing, cold storage, and freezing of the catch, and repairing fishing vessels and nets [1]. Consequently, the high concentration of human activity, combined with unregulated discharge, creates significant uncertainty in the ecological environment of fishing ports. Monitoring and evaluating the water environment quality of fishing ports and clarifying the eutrophication status of water bodies are the key to the comprehensive management of the fishing port environment, which is of great practical significance [3,4].

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Fisheries constitute a crucial pillar of Hainan Province's economy. In 2022, the total economic output of the fishery industry in Hainan was 56.596 billion yuan [5]. By the end of 2019, the province had approximately 25,000 motorized fishing vessels and a maritime fishing population of about 335,000. The annual marine catch was 1.079 million tons, with around 700,000 tons of fish unloaded at ports each year. The aquatic product processing capacity reached 368,000 tons, of which 186,000 tons were seawater-processed products [5]. Hainan Island encompasses 68 bays of various sizes available for development, with 43 of these included in the Ministry of Agriculture's registry of fishing ports. Currently, most fishing ports in Hainan are naturally formed bays or coves characterized by strong enclosure and limited water exchange, leading to rising concerns about environmental pollution. In recent years, several scholars have investigated the water quality in various fishing ports across Hainan Province, such as Xincun Port [6], Xiaohai [7], Haitou Port [8], Baimajing [9]. However, no comprehensive monitoring and evaluation have been conducted on the primary fishing ports of Hainan Province. This study targets ten major fishing ports in Hainan Province, including six central fishing ports and four first-class fishing ports. Water samples were collected to analyze seawater quality indicators, assess the pollution levels of primary contaminants, and utilize the eutrophication index to determine the nutrient enrichment status.

2 Materials and methods

2.1 Study areas and sample collection

This study focuses on ten major fishing ports in Hainan Province, including six central fishing ports and four first-class fishing ports. Seawater samples were collected in April 2022. The locations of the sampling points are depicted in Table 1.

Table 1. Information on the locations of different fishing ports.

Location	Longitude	Latitude	Description
FP1	109°7'29''	18°21'33''	Yazhou Central Fishing Port in Sanya
FP2	108°41'45''	18°41'2''	Lingtou First-Class Fishing Port in Ledong
FP3	108°38'37''	19°6'58''	Basuo Central Fishing Port in Dongfang
FP4	108°48'37''	19°25'43''	Haiwei First-Class Fishing Port in Changjiang
FP5	109°12'58''	19°43'8''	Baimajing Central Fishing Port in Danzhou
FP6	109°31'13''	19°53'13''	Xinying Central Fishing Port in Lingao
FP7	110°34'28''	20°1'42''	Puqian Fishing Port in Wenchang
FP8	110°36'59''	19°14'23''	Tanmen Central Fishing Port in Qionghai
FP9	110°30'30''	18°53'40''	Gangbei First-Class Fishing Port in Wanning
FP10	109°58'12''	18°24'53''	Xincun Central Fishing Port in Lingshui

2.2 Instrumental analysis

The collection, pretreatment, and preservation of all samples were conducted in accordance with the Marine Monitoring Specifications (GB/T12763-2007) and the Marine Monitoring

Standards (GB17378-2007). The study monitored several indicators, including Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand using permanganate (COD), Chlorophyll a (Chl a), Ammonium (NH_4-N), Nitrite (NO_2-N), Nitrate (NO_3-N), and Dissolved Inorganic Phosphate (DIP). Dissolved Inorganic Nitrogen (DIN) in seawater is the sum of NH_4-N, NO_2-N, and NO_3-N. The specific analysis items and methods are as follows: COD was analyzed using the alkaline potassium permanganate oxidation method. Chl a was measured by spectrophotometry (SL 88-2012). NH_4-N was determined by the Nessler's reagent spectrophotometry method (HJ536-2009). NO_2-N was measured using the phenol disulfonic acid spectrophotometry method (GB/T7480-1987). NO_3-N was analyzed using the zinc-cadmium reduction method (HJ346-2007). DIP was analyzed using the ascorbic acid reduction phosphomolybdenum blue method (HJ671-2013).

2.3 Evaluation of seawater quality

The BOD_5, COD, DIN, DIP and other parameters of seawater were evaluated according to the water quality standard of 'Seawater Quality Standard' (GB3097-1997). This assessment aims to analyze the pollution status of the main parameters in the studied sea area. The evaluation method employed is the single-factor pollution index method. The equation (1) is on below.

$$P_i = C_i/S_i \qquad (1)$$

Where P_i is the single-factor pollution index for each parameter in the seawater, reflecting the degree of pollution of the i-th parameter. C_i is the measured concentration sum of each parameter. S_i is the corresponding limit value for the fourth category of seawater quality standard from the Seawater Quality Standards (GB3097-1997).

2.4 Assessment of water quality nutrient levels

The eutrophic state of the water body in the study area was evaluated using the Eutrophication Index (E). The formula for calculating the Eutrophication Index is given below in Equation (2).

$$E_i = \rho(COD) \times \rho(DIP) \times \rho(DIN) \times 10^6/4500 \qquad (2)$$

Where E_i is the Eutrophication Index. $\rho(COD)$ is the concentration chemical oxygen demand of the seawater (mg/L). $\rho(DIN)$ is the concentration of dissolved inorganic nitrogen (mg/L). $\rho(DIP)$ is the concentration of dissolved inorganic phosphate (mg/L). According to the E_i values, the eutrophication levels were classified as follows in Table 2[10].

Table 2. The classification of eutrophication levels.

E_i values	eutrophication levels
E_i <1	Oligotrophic (poor in nutrients)
1< E_i <2	Mildly Eutrophic
2< E_i <5	Moderately Eutrophic
5< E_i <15	Highly Eutrophic
E_i >15	Severely Eutrophic

3 Results and discussion

3.1 Analysis of sea water quality indicators

Various parameters among various fishing ports in Hainan Province are depicted in Table 3.

Table 3. Statistical summary of various parameters in different fishing ports.

Location	BOD_5 (mg/L)	COD (mg/L)	Chl a (mg/L)	NH_4-N (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)	DIN (mg/L)	DIP (mg/L)
FP1	6.40	8.00	10.00	0.27	0.13	8.00	0.40	0.20
FP2	6.70	8.50	2.00	0.08	0.17	5.00	0.25	0.05
FP3	7.20	8.50	＜2.00	0.38	3.72	64.00	4.17	0.18
FP4	7.00	8.20	＜2.00	0.06	0.15	11.00	0.22	0.08
FP5	6.70	8.00	＜2.00	0.36	0.01	238.00	0.61	0.52
FP6	6.30	7.90	＜2.00	0.12	0.68	11.00	0.81	0.08
FP7	7.00	8.20	＜2.00	0.13	0.04	2.00	0.17	0.10
FP8	6.50	8.00	10.00	0.26	0.53	12.00	0.80	0.16
FP9	6.00	7.20	2.00	0.09	0.22	11.00	0.32	0.38
FP10	6.90	8.20	＜2.00	0.19	0.05	2.00	0.24	0.07

As indicated in Table 3, there are significant differences in the water quality indicators among various fishing ports in Hainan Province. The range of seawater BOD_5 spans from 6.00 to 7.20 mg/L, with the highest value recorded at Basuo Port in Dongfang. The range of COD spans from 7.20 to 8.50 mg/L, with the highest values appearing at both Basuo Port in Dongfang and Lingtou Port in Ledong. These high COD and BOD_5 values at Basuo Port in Dongfang can be attributed to the dense population, bustling commerce, and proximity of seafood markets influenced heavily by human activities. In densely populated areas, domestic sewage and industrial wastewater have complex sources, containing a large amount of organic matter, and high nitrogen and phosphorus substances. Unorganized discharge and inadequate treatment of domestic sewage and sewage from wharf treatment fishing are easily discharged into the port, thus increasing the content of organic matter in the water. The concentration of chlorophyll a ranges from less than 2.00 to 10.00 mg/L, with the highest values found at Yazhou Fishing Port in Sanya and Tanmen Fishing Port in Qionghai. The presence of abundant nutrients alongside favorable water temperature and light conditions facilitates prolific algae growth. The concentration of DIN in seawater ranges from 0.17 to 4.17 mg/L, with the highest value detected at Basuo Port in Dongfang. The NH_4-N concentration varies between 0.06 and 0.38 mg/L, while NO_2-N ranges from 0.01 to 3.72 mg/L, and NO_3-N ranges from 2.00 to 238.00 μg/L. The concentration of DIP ranges from 0.05 to 0.52 mg/L, with the highest value recorded at Baimajing Fishing Port in Danzhou. The maximum DIP concentration at Baimajing Fishing Port is attributed to its proximity to densely populated town areas, where pollutants from human activities and aquaculture are discharged into the water [9].

3.2 Water quality of sampling sites

The parameters BOD_5, COD, DIN, and DIP of the seawater were evaluated against the Class IV standards stipulated in the Seawater Quality Standards (GB3097-1997), which are applicable to marine port areas and marine development zones. The seawater quality parameters were evaluated based on the equation (1), the single factor pollution indices of major pollutants in different fishing ports are presented in Table 4. As indicated in Table 4, the assessment of key pollutants in the seawater from various fishing ports in Hainan Province reveals that the overall water quality was suboptimal during the sampling period. The observed levels of COD and BOD_5 at sampling points in different fishing ports exceeded the Class IV seawater quality standards. BOD_5 level at Basuo Port in Dongfang exceeded the standard by 1.44 times and COD level exceeded 1.70 times. DIN levels at Baimajing Port in Danzhou exceeded the standard by 2.03 times, followed by Xinying Port in Lingao and Tanmen Port in Qionghai, both exceeding the standard by 1.60 times. DIP exceeded the Class IV seawater quality standards in all fishing port samples, with Baimajing Port in Danzhou exceeding by 11.56 times, and Gangbei Port in Wanning by 8.44 times. Wanning Xiaohai is the largest lagoon inner sea in Hainan, which is greatly affected by tidal transport and river runoff transport in the South China Sea [7]. These results indicated significant seawater pollution in Hainan Province's fishing ports during the sampling period. The selected sites are predominantly naturally formed bays or coves with limited hydrodynamic exchange capacity [7,10]. These ports are characterized by the intersection of industrial and residential activities, significantly impacted by human activities, including the increase in the number of over-standard discharges from land-based sewage outlets into the sea [11], domestic sewage and agricultural non-point source pollution [7].

Table 4. Single factor contaminant index of major pollutants in different fishing ports.

Location	BOD_5 (mg/L)	COD (mg/L)	DIN (mg/L)	DIP (mg/L)
the Class IV standards	5.00	5.00	0.50	0.045
FP1	1.28	1.60	0.80	4.44
FP2	1.34	1.70	0.50	1.11
FP3	1.44	1.70	2.03	4.00
FP4	1.40	1.64	0.44	1.78
FP5	1.34	1.60	0.77	11.56
FP6	1.26	1.58	1.61	1.78
FP7	1.40	1.64	0.33	2.22
FP8	1.30	1.60	1.60	3.56
FP9	1.20	1.44	0.63	8.44
FP10	1.38	1.64	0.48	1.56

3.3 Eutrophication levels at sampling sites

The Eutrophication Index (E) results for seawater at various fishing ports in Hainan Province are presented in Table 5. Inshore nutrient pollution is a common problem. With the increase of land-based pollutant emissions, the eutrophication of coastal waters is increasing. As depicted in Table 5, the phenomenon of eutrophication in the seawater of different fishing ports in Hainan Province is quite severe, with the eutrophication index (E) ranging from 2.38 to 56.29. The eutrophication index is higher than that of Zhanjiang Port [12], Huanghua Port [13] and Pearl River Estuary [14], lower than that of the Heiyanzi Central Fishing Port and Yangkou Central Fishing Port [13]. Sampling sites at Baimajing Central Fishing Port in

Danzhou, Basuo Central Fishing Port in Dongfang, Tanmen Central Fishing Port in Qionghai, and Gangbei First-Class Fishing Port in Wanning exhibit the eutrophication index greater than 15, indicating severe eutrophication. Among them, the eutrophication index of central fishing port of Baimajing is 56.29, and the sampling point is located at the wharf. The water quality is directly related to the discharge of domestic sewage into the sea [9]. Sampling sites at Yazhou and Xinying Port have the eutrophication index between 5 and 15, denoting high eutrophication. The remaining sites, with the eutrophication index between 2 and 5, are classified as moderately eutrophic. It is close to the Liaodong Bay [15].

Table 5. The eutrophication index of different fishing ports.

Location	the eutrophication index	Eutrophication level
FP1	14.22	Highly Eutrophic
FP2	2.38	Moderately Eutrophic
FP3	34.58	Severely Eutrophic
FP4	3.24	Moderately Eutrophic
FP5	56.29	Severely Eutrophic
FP6	11.32	Highly Eutrophic
FP7	3.02	Moderately Eutrophic
FP8	22.70	Severely Eutrophic
FP9	19.15	Severely Eutrophic
FP10	3.09	Moderately Eutrophic

4 Conclusions

The nutrient concentrations in seawater vary markedly across different fishing ports. During the sampling period, water quality was poor: COD and BOD_5 levels at various sampling points exceeded Class IV seawater quality standards, with Basuo Port in Dongfang showing the highest levels, where BOD_5 exceeded the standard by 1.44 times and COD by 1.7 times. DIN levels exceeded the standard by 2.03 times at Danzhou Baimajing Port, followed by Xinying Port in Lingao and Tanmen Port in Qionghai, both at 1.60 times the limit. DIP concentrations in seawater samples from all fishing ports significantly exceeded Class IV seawater quality standards, with Baimajing in Danzhou exceeding the standard by 11.56 times. The Eutrophication Index indicates that eutrophication is quite severe, which warrants significant concern and immediate attention.

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